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STUDIES ON IONIC EXCHANGE

WITH SPECIAL REFERENCE TO THE CONDITIONS IN SOILS

By

LAMBERT WIKLANDER

Reprinted from

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Studies on Ionic Exchange

with Special Reference to the Conditions in Soils.

By LAMBERT WIKLANDER.

From the Institute of Pedology.

Preface.

The present investigation was started in 1939. The greater part of it was carried out at the Institute of Pedology and the remaining part at the Analytical Laboratory of the Royal Agricultural College of Sweden.

Having finished my investigations I wish to express my gratitude to those who helped me in my work. First of all I address myself to Professor SANTE MATTSON, Director of the Institute of Pedology, who for the past ten years has been my inspiring teacher in soil science and colloid chemistry. For the invaluable support that Professor MATTSON has given by discussions and advice and by allowing me to use the equipment of the Institute I wish to express my sincere gratitude.

I am indebted to Professor OLOF SVANBERG, Director of the Chemical Institute and Analytical Laboratory, for his kindness in allowing me to use the equipment necessary for my investigation during the time I worked as an assistant at the Analytical Laboratory.

I would also express my appreciation of interesting discussions with Agronom NILS KARLSSON. As an assistant at the Institute of Pedology Mr. KARLSSON did me a great many services, for which I am grateful.

Further I am indebted to Fil. Dr. LARS FRYKHOLM, Head of the college library, and to Fil. Kand. ASTRID GUILLETMOT, Library assistant, for their unfailing helpfulness in procuring the necessary books and papers,

and to Mr. KARL ODENGRIM, who on some occasions assisted me in making certain analyses,

and to Dr. Jur. WILHELM HEINEMANN, who did the main part of the translation.

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Uppsala, September 1946.

Lambert Wiklander.

Contents.

Part I. Introduction 4

Part II. The Physico-Chemical Basis of Exchange Reactions 5

1. Short Historical Survey of the Development of the Conception of Ionic Exchange 5
2. Ionic Radius and Ion Hydration 8
3. The Activity Concept 11
4. The Structure of the Micelle 18
5. The Crystalline Structure of Clay Minerals 21
6. The Chemical and Physical Nature of the Surface Complex .. 26
7. The Strength of Acidoids and Basoids 31
8. Neutralization Curves and Cation Exchange Capacity 33
9. The Application of the Activity Concept to Colloids 34
10. The Donnan Equilibria 37

Part III. The Relative pH-Reducing Power of the Alkali and Alkaline-Earth Ions in Electrodialysed Materials 43

1. Introduction 43
2. Theoretical Points of View 46
3. Materials Investigated: Humus, birch leaves, aluminium phosphate, ferriphosphate, aluminium silicates, ferrisilicate, permutite, bentonite, kaolinite, bleaching earths, and four mineral-soils 48
4. Experimental Methods 50
5. Time Necessary for the Accomplishment of the Equilibrium .. 52
6. Experimental Results 54
   A. pH in neutral salt solutions 54
   B. Neutralization curves 72
7. Conclusions 78

Part IV. General Properties of a Resin Acidoid and Basoid 79

1. Introduction 79
2. The Cation Exchange Resin Wofatit K 80
   A. Contents of S, Fe and N 81
   B. Time necessary for wetting 81
   C. Solubility in water 82
   D. Mechanical stability in water 83
   E. Time required for ionic exchange equilibrium 84
   F. Neutralization curves in water and in 1.0 N. solutions ... 86

3. The Anion Exchange Resin Wofatit M 87
   A. Contents of N 87
   B. Solubility in water 88
   C. Neutralization curves in water and in 1.0 N. solutions and pH in solutions of KCl and K_2SO_4 88

Part V. The Relationship between the Replacing Power of the H-ion and the Acidoid Strength and the Position of this Ion in the Lyotropic Series ... 92
1. Introduction ... 92
2. Description of the Ion Exchangers Studied ... 94
A. The resin Wofatit K ... 94
B. Permutite ... 94
C. Vårdsberg clay ... 94
D. Ordinary bath sponge ... 95
3. Experimental Methods ... 96
4. Experimental Results ... 97
A. The resin Wofatit K ... 97
B. Permutite ... 100
C. Vårdsberg clay ... 100
D. Ordinary bath sponge ... 102
5. Conclusions ... 103

Part VI. Amphoteric Reactions of an Aluminium Phosphate Complex ... 104
1. Theoretical Considerations ... 104
2. Experimental Results ... 105

Part VII. The Effect of Dilution on Exchange Equilibria ... 107
1. Introduction ... 107
2. Experimental Results ... 109
A. Alkalimetric determination of the exchange acidity in the systems: ... 109
a. H-resin + chloride solutions of Li, Na, K, Mg, Ca, and Ba at low concentrations. (Determination of the volume of the micellar solution.) ... 109
b. H-resin + chloride solutions of Li, Na and K at higher concentrations ... 112
B. The influence of the change in volume on the equilibrium of the systems: ... 112
a. NH_4-Ca-resin + HCl ... 112
b. Cl-SO_4-resin + NaOH ... 113
C. Leaching of H-resin with neutral salt solutions of various concentrations and determination of adsorbed ions: ... 114
a. System NH_4-K-resin + NH_4Cl + KCl ... 115
b. System NH_4-Ca-resin + NH_4Cl + $CaCl_2$ ... 115
3. Conclusions ... 118

Part VIII. The Influence of Heating on the Exchangeability of the Adsorbed Ions ... 119
1. Introduction ... 119
2. Experimental Methods ... 120
3. Experimental Results ... 122
A. Permutite ... 122
B. Vårdsberg clay ... 123
4. Discussion ... 124

Part IX. The Influence of the Degree of Saturation of the Exchanger and of the Nature of the Complementary Ions on the Exchangeability of Adsorbed Ions ... 125
1. Introduction ... 125
2. Theoretical ... 127

3. Experimental Methods 138
4. Analytical Methods 140
5. Experimental Results 141

A. Replacement of cations from an acidoid resin 142
Series: a. Li-NH_4; b. Na-NH_4; c. K-NH_4; d. Mg-NH_4; e. Ca-NH_4; f. Ba-NH_4; g. La-NH_4; h. Ca-K; i. K-NH_4; j. Ca-Mg; k. Ca-NH_4.
B. Replacement of SO_4- and Cl-ions from a basoid resin 150
C. Replacement of cations from permutite 150
Series: a. NH_4-Na; b. K-Na.
D. Replacement of cations from Vårdsberg clay 152
Series: a. Ca-NH_4. (Study of the ammonia fixation in the soil);
b. Ca-NH_4;
c. Ca-K. (Study of the potassium fixation in the soil);
d. Ba-Mg.

6. Conclusions 154

Part X. Summary for Parts II—IX 158

Part XI. References 164

I. Introduction.

The present investigation deals with the ionic exchange in certain materials of importance to agriculture.

The following problems have been studied:

1. the relative pH-reducing effect of the alkali and alkaline-earth ions in different ion exchanging substances;
2. general properties of a resin acidoid and basoid;
3. the relation between the replacing power of the H-ion on one side and the nature of the ion exchanging material (the acidoid) on the other and, in connection with this, the position of the H-ion with regard to its replacing power in relation to that of the alkali and alkaline-earth ions;
4. the amphoteric reactions of an »isoelectrically» precipitated aluminium phosphate;
5. the effect of dilution on the ion exchange equilibria in a resin acidoid and basoid;
6. to what an extent an increase in temperature influences the exchangeability of the ions in electrodialysed permutite and clay after saturation with alkali and alkaline-earth hydroxides;
7. if there is some connection between the degree of saturation of an ion exchanger with a certain ion and the exchangeability of the ion in question, and if any such connection is influenced by the character of other ions present.

In part II of this paper, a description is given of the activity concept, the structure of the ion exchangers, the general laws of ionic exchange, and of such factors as might influence ionic exchange; all these questions are dealt with to such an extent as seems justified by the experiments and their interpretation. Certain results of research have been discussed as far as they were of interest for this investigation; these discussions will be found, partly in the general review at the beginning of this paper, partly in connection with the treatment of the above questions.

The ion exchange material at my disposal in the beginning of these investigations consisted of weak acidoids and basoids exclusively. The intention was to study ion exchange even in strong acidoids and basoids but these turned out to be very difficult to procure. Sulphite cellulose is a strong acidoid and has been the object of thorough examination by Du Rietz (1938). The disadvantage of this substance lies in its low ion exchange capacity which made it less suitable for my purposes. However, I gradually succeeded in procuring synthetic ion exchange resins, *Wofatit K* and *Wofatit M*, both with high exchange capacity. The former is exclusively a cation exchanger, the latter in the first hand an anion exchanger; by their other properties they were extremely well suited for the intended investigations.

The ion exchanging materials which were examined consisted of:

1. natural ion exchangers: electrodialysed humus, ordinary bath sponge, electrodialysed clays, bentonite, kaolinite and activated bleaching clays;
2. synthetic ion exchangers: »isoelectrically» precipitated silicates and phosphates of aluminium and iron, permutite and resins.

II. The Physico-Chemical Basis of Exchange Reactions.

1. Short Historical Survey of the Development of the Conception of Ionic Exchange.

To save space, only some of the most important names and dates shall be quoted.

According to Sestini (1873), as early as 1819, the Italian chemist Gazzeri showed that clay decolourates liquid manure and keeps back its soluble substances which gradually are delivered to the plants.

The Englishman THOMPSON, however, must be regarded as having been the first to examine more or less systematically the capability of soils to adsorb inorganic salts. In 1845 he found by means of experiments which were not published until five years later that, when soil was mixed with ammonium salts and then leached with water, a great part of the ammonia was kept back (THOMPSON 1850).

According to WAY (1850), HUXTABLE showed in 1848 that liquid manure, when filtered through soil, looses both colour and smell. Referring to this, WAY writes: »In fact, that it went in manure and came out water.» Later, FORCHHAMMER (1850) has pointed out that clays release calcium and magnesium when leached with sea-water.

Inspired by the results of THOMPSON and HUXTABLE, the English chemist WAY (1850, 1852) took up these problems by systematic and very fruitful studies. On this occasion, he made the important discovery that soils keep back the bases of an added easily soluble salt and release an equivalent amount of lime. WAY studied base exchange phenomena of this kind in synthetic aluminium silicates and drew the conclusion that the base exchange in soil is restricted to the clay fraction and connected with the double silicates.

After the publication of these pioneer works ion exchange and problems connected with it have been the subject of intense studies in many countries. At first, attempts were made to interpret the ion exchange equilibrium quantitatively with the aid of empirical formulas of such a kind as to harmonize with the experimental results. One of the oldest and best known of these formulas is the adsorption isotherm of FREUNDLICH (1930):

$$\frac{x}{m} = k \cdot c^p$$

where x signifies the adsorbed amount of ions or molecules per m g of the adsorbing substance; c is the concentration of the solute in the equilibrium solution and k and p are two constants which are dependent on the temperature and the nature of the reacting substances. At first, the formula was meant by FREUNDLICH to be used for apolar adsorption but later it was applied even to exchange adsorption. The formula represents a parabola and does not give a definite limit for the exchange capacity.

Starting on the assumption that the ion equilibrium between permutite and solution is not influenced by dilution, WIEGNER (JENNY 1927) has modified the adsorption isotherm of FREUNDLICH into an exchange isotherm:

$$y = k \cdot \left(\frac{c}{a - c}\right)^p,$$

where c, k and p have the same meaning as in FREUNDLICH's formula while a is the initial concentration of the added solute and y the amount of ions exchanged per g permutite.

In order to determine the manure requirement of the soil, VAGELER (1932) has published an empirical formula of hyperbola-like form:

$$y = \frac{x \cdot T}{x + q \cdot T},$$

where y is the amount of the replaced cations, T the total exchangeable amount of the same cation, x the amount of the replacing cation added in the beginning of the experiment, and q a constant.

In the above mentioned formulas no consideration is apparently paid to the valence and the displacement of the equilibrium, which may take place between ions of different valence, when the system is diluted with water. Referring to theoretical considerations, ROTHMUND and KORNFELD (1918) on the other hand maintain that the equilibrium for ions of different valence is a function of, among other factors, the dilution. For particulars concerning this question see part VII. Working with permutite ROTHMUND and KORNFELD started on the assumption that the relation between the amounts of two ions on permutite was a function of the amounts of the ions contained in the solution. They described the equilibrium conditions for ions of the same valence by an empirical formula which can be suitably written:

$$\frac{A_i}{B_i} = k \cdot \left(\frac{[A]}{[B]}\right)^p$$

In this formula A_i and B_i express the amounts of the cations A and B on the permutite and $[A]$ and $[B]$ the concentration in the solution; k is a proportionality constant, and p a constant which is aimed at better adjusting the formula to the experimental curves. In spite of the fact that ROTHMUND and KORNFELD denied the validity of the law of mass action for the ion exchange in permutite, it can be stated that their formula is based on this law which, however, is somewhat modified by the index p.

MØLLER (1935) went one step farther than ROTHMUND and KORNFELD when, from a chemical point of view, he fully applied the law of mass action, proposing the use of activity instead of concentration. Naturally, MØLLER could only calculate the activity in the outside solution. His application of the law of mass action for judging the experimental results achieved with the synthetic ion exchanger Natrolith can be generally described by the formula:

$$\frac{A_i^{n_B}}{B_i^{n_A}} = k \cdot \frac{(A)^{n_B}}{(B)^{n_A}},$$

where A_i and B_i have the same meaning as in the preceding formula, (A) and (B) signify the activity of the cations A and B in the equilibrium solution, n_A and n_B are the valence for A and B respectively, and k is a proportionality constant, the so called exchange constant.

Before MØLLER, but not to the same extent, KERR (1928), VANSELOW (1932), and GAPON (1933) had used exchange formulas which were founded on the law of mass action.

Also other investigators as DAMSGAARD-SØRENSEN (1941) and SAMUELSON (1944) have, in the same way as MØLLER but with use of concentration in the solution, applied the law of mass action for the interpretation of the ion exchange equilibrium. Working with dilute systems, MØLLER found constant k-values, but these observations are far from being universally valid, judging from the results of DAMSGAARD-SØRENSEN.

The next step in the development from the empirical formulas towards the strictly theoretically founded formulas is taken when, in MØLLER's formula, the concentration of cations on the ion exchanger is replaced by activity, while at the same time k gets the value 1. In this way, the well-known so called Donnan-equilibrium is obtained which, in order to demonstrate the likeness with the preceding formula, can be expressed in the following way:

$$\frac{(A)_i^{n_B}}{(B)_i^{n_A}} = \frac{(A)_s^{n_B}}{(B)_s^{n_A}};$$

i and s signify ion exchanger and solution respectively.

On account of the great importance of the Donnan-equilibrium for the study of ionic exchange reactions, it seems to be adviceable not to enter into a detailed discussion before the activity concept and the structure of the ion exchanger have been dealt with.

2. Ionic Radius and Ion Hydration.

In connection with the study of ion exchange, it is of interest to distinguish between the concepts of the absolute or crystallographic ionic radius and of the »radius» of the hydrated ion, the so called electrodynamical ionic radius. By regarding the ions in a crystal as compact spheres, GOLDSCHMIDT (1927) has been able to determine the absolute size of a great number of cations and anions. The same has been done by PAULING (1927) with the aid of theoretical calculations. The results of both investigators regarding the crystallographic radius of the alkali and alkaline-earth ions are in good agreement as is to be seen from the following table:

Table 1. *Ionic radii in Å, according to Goldschmidt and Pauling.*

	NH_4^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	La^{3+}
Goldschm..	1.43	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43	1.22
Pauling ...	—	0.60	0.95	1.33	1.48	1.69	0.65	0.99	1.13	1.35	1.15

In order to explain several chemical and physical properties of salts in aqueous solution it has been assumed that the ions in aqueous solution are hydrated. This assumption is supported by thermodynamical considerations (see VAN ARKEL and DE BOER 1931). A picture of the hydration mechanism is presented by these authors.

Since the ions surround themselves with a strong electric field, they cause an additional polarization of the surrounding water dipoles. These become attracted and adjust themselves into a strongly bound »sphere». The induced polarization and orientation of the water molecules rapidly decreases in the outward direction, so that only the most inwardly situated molecules might be regarded as strongly bound. The hydration increases with the charge of the ion and decreases with growing crystallographic radius. In accordance with this, it appears from the preceding table that the degrees of hydration for the alkaline ions must be arranged in the following order:

$$Li > Na > K > Rb > Cs$$

and for the alkaline-earth ions:

$$Mg > Ca > Sr > Ba.$$

The charge in each series is the same, but the radius increases.

In the same order lies the electrodynamic radius of the ions, which is indicated by the ionic velocities.

The hydration is measured by the *hydration number* which gives the number of water molecules bound per ion. The determination of the hydration number has proved very difficult. Many investigations have been made but the results did not always show the conformity that was to be desired.

ULICH (1933) who has thoroughly studied ion hydration distinguishes, on account of the great difference in binding strength, two forms of hydration, an »engere» or chemical and a »weitere» or physical hydration. In the former type the water molecules are so strongly bound that the whole complex acts as a stable compound or a »molecule», for instance in the case of ion migration. The limit between chemical and physical hydration is drawn by ULICH in such a way that, in the case of the former, the water molecules

cannot become loosened by thermic motion of the molecules but in exceptional cases; this, on the other hand, is the case with the latter.

Ulich (1933) defines the hydration number by the number of »enger» bound molecules. According to Ulich this number can be determined by five fundamentally different methods and, generally, with very good conformity. The following table gives the values for some ions which are the most probable ones for the chemical hydration in dilute solutions at room temperature.

Table 2. *Most probable hydration numbers according to Ulich.*

Ion	H_3O^+	Li^+	Na^+	K^+	Rb^+	Ag^+	Mg^{++}	Ca^{++}	Ba^{++}	Zn^{++}
Hydration number	3[1]	6	4	2.5	2	3.5	9–13	8–10	6–8	11–13
Ion	Fe^{++}	Cu^{++}	Cd^{++}	Pb^{++}	F^-	Cl^-	Br^-	J^-	ClO_4^-	NO_3^-
Hydration number	11–13	11–13	10–12	5–7	5	3	2	0.5	0	2

The hydration of the H-ion is thought to take place in such a way that the proton unites with one molecule of water forming the stable hydroxonium-ion. As regards volume, the H_3O^+ has a position between Na^+ and K^+ and, therefore, becomes hydrated by three additional molecules of water.

Other investigators (Du Rietz 1938) obtained higher hydration values, but this can be due to the fact that even physical hydration water is included in the final figures. But even if the absolute hydration figures in some cases are different from those mentioned above, the mutual order is nevertheless unchanged. The hydration number is likely to vary with the concentration, the temperature, and the intensity of the electrostatic forces which are at work between the ions. Oppositely charged ions may in certain cases be able to penetrate through the hydration envelope. This, for instance, may be the case at ion association. (See the following chapter.) It might be pointed out in this connection that even the colloid ions are more or less hydrated. The greater the density of charge of the colloid ion, the stronger is the hydration.

When the monovalent and divalent hydrated ions are arranged by increasing volume, the following series is obtained:

$$K < Na < Li < Ba < Sr < Ca < Mg.$$

[1] In all 4 H_2O on 1 H^+.

The mutual order between the monovalent ions and between the divalent ones is often called the *lyotropic series*.

The crystallographic radius of ions in solution is of interest so far as it, together with the charge, determines the hydration and, in certain cases, seems to be the decisive factor for the replacing power of an ion and for the fixation of ions in a non-exchangeable form in the crystal lattice. The electrodynamic radius is of the greatest interest when the activity coefficients of the ions are calculated and in the case of diffusion and ionic exchange in general.

3. The Activity Concept.

In the study of ion exchange reactions it is important to take account of the effective concentration of an ion and to understand in which way this effective concentration is dependent on the charge and the volume of the ion and on the kind and concentration of other ions present. The modern conception of electrolytes will therefore be briefly treated in this chapter as far as it has a bearing on the problems and questions dealt with in this paper.

In contrast to the classical theory of electrolytes, the modern theory considers the strong electrolytes as being completely dissociated. In certain cases however, ions of opposite charge may unite into an ion pair. This so called ion association will be discussed later. Between the ions electrostatic forces (the interionic forces) are at work, which cause an ion to surround itself with more ions of the opposite than of the same charge. The electrolyte in solution thus tends to assume a similar structure as in a crystal lattice.

In order to explain the deviation of the strong electrolytes from the classical laws, Lewis (Lewis and Randall 1923), Milner, Bjerrum, Brønsted, Debye and Hückel, and others (see Falkenhagen 1932) have developed the theory of the relationship between activity (= effective concentration), activity coefficient (f) and ionic strength (μ). With the aid of these concepts attempts have been made to master the interionic forces which are at work between the ions in a solution, thus opening a possibility for the application of the classical laws to the strong electrolytes. Both the activity and the mobility of the ions are influenced by the interionic forces. This effect becomes the stronger, the higher the concentration. Even in solutions of medium strong electrolytes the interionic forces become evident in the same way. These, however, do not here become so pronounced on account of the low ion concentration resulting from the incomplete dissociation. As we will see later, the degree of protolysation[1] (Brønsted 1943, Kolthoff 1944) of

[1] According to the concept of Brønsted an acid (HA) is protolysed in water in the following way:

$$HA + H_2O \rightleftarrows H_3O^+ + A^-$$

weak acidoids and basoids is influenced to a great extent by the electrostatic forces emanating from the strong electrolytes. The activity of undissociated molecules is only slightly affected because they lack a charge.

The activity (**a**) is usually defined as the product of the activity coefficient (f) and the concentration (c):

$$\mathbf{a} = f \cdot c.$$

If the cation activity is expressed by $\mathbf{a}_+$ the anion activity by $\mathbf{a}_-$ and the mean ionic activity by $\mathbf{a}_\pm$, the following formula is valid for a binary electrolyte:

$$\mathbf{a}_\pm = \sqrt{\mathbf{a}_+ \cdot \mathbf{a}_-}$$

In infinitely dilute solutions the interionic forces can be neglected. In this case, activity may be considered equal to concentration, and the activity coefficient thus becomes = 1. On the other hand, when concentration increases, f decreases but may, in certain cases, pass through a minimum at relatively high concentrations and then increase to values above 1 as the concentration is further increased, compare fig. 2 and 3.

When the ionic strength of a solution is determined, not only the concentration but even the valence of the ions must be taken into consideration. Thus, the ionic strength expresses, to a certain extent, the magnitude of the interionic forces. The mean ionic strength in a solution containing ions of the types A, B, C . . . with the charges n_A, n_B, n_C . . ., and the molar concentrations c_A, c_B, c_C . . . is determined by the following expression:

$$\mu = \tfrac{1}{2}\,(c_A \cdot n_A^2 + c_B \cdot n_B^2 + c_C \cdot n_C^2 + \ldots) = \tfrac{1}{2}\,\Sigma\, c \cdot n^2.$$

The equilibrium is given by the expression:

$$\frac{[\overset{+}{H_3O}]\,[\overset{-}{A}]}{[HA]\,[H_2O]} = k\,,$$

where bracket designates concentration and k is the protolysis constant. The hydrated proton, H_3O^+, is often called hydronium ion but in the following it will as usual be called hydrogen ion. Since in dilute solutions the water concentration is practically constant, the equation above may be written:

$$\frac{[\overset{+}{H_3O}]\,[\overset{-}{A}]}{[HA]} = k_s\,,$$

where k_s is identical with the classical dissociation constant, the apparent or stoichiometric constant. From what has been said, it appears that the new conception of protolysis and protolysis degree of acids correspond to the classical conception of dissociation and degree of dissociation.

At a high degree of dilution it is mainly the ionic strength of the solution which, besides the valence, determines the activity coefficient of an ion. DEBYE and HÜCKEL (1923) have electrostatically deduced a mathematical relationship between f and μ in highly dilute solutions. When water is used as a solvent and at a temperature of 20° C the *mean activity coefficient* of an electrolyte is calculated by the approximative formula:

$$-\log f_{\pm} = pf_{\pm} = 0.5 \cdot n_{+} \cdot n_{-} \cdot \sqrt{\mu} \qquad (1)$$

In analogy to this, the activity factor for an ion i with the valence n_i is obtained from the formula:

$$-\log f_i = pf_i = 0.5 \cdot n_i^2 \cdot \sqrt{\mu} \qquad (2)$$

DEBYE and HÜCKEL, on deriving their theory, assumed that an ion surrounds itself with a swarm of ions of opposite charge. It forms the center of an oppositely charged ion atmosphere. For this reason, when the f-value of an ion is calculated, greater weight ought to be attached to oppositely charged ions and, instead of the mean ionic strength, a cation- or anion-strength ought to be used, because the interionic forces are stronger between ions of opposite than of the same charge. The investigations of BRØNSTED (1922) on the solubility of salts and HASS' and JELLINEK's (1932) electrometrical determinations of activity coefficients for some ions indicate that the valence and the ionic radius of the ions which are charged oppositely to the central ion, exert a much greater influence on the activity coefficient of this ion, than do the ions of the same sign of charge. This effect begins already in dilute solutions. DU RIETZ (1936) has suggested a way to calculate the cation- and anion-strength approximatively.

It follows from formula (2) that, with increasing ionic strength, f decreases the faster, the higher the valence. Therefore, the activity coefficient of a polyvalent ion undergoes greater variations than that of a monovalent ion, when the ionic strength is varied, cf. fig. 3.

The limiting formula deduced by DEBYE and HÜCKEL is valid only at very low ionic strength values. It is usually considered to give satisfactory results at ionic strength values up to 0.01 but, above this limit, the divergences become considerable. By paying attention to the ionic radius, however, DEBYE and HÜCKEL succeeded in obtaining from their deductions a simple formula the validity of which extends to ionic strength values of about 0.1. When the distance of the closest approach of the opposite charged ions is called a, formula (2) can be replaced by the following more exact expression:

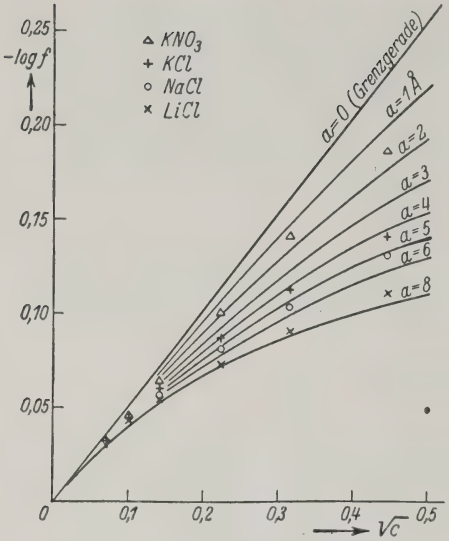


Fig. 1. The relation between pf for uni-uni-valent salts and the square root of the concentration. Theoretical curves at different minimum ion distances (a) as well as experimental values at 25° C, according to Ulich (1933).

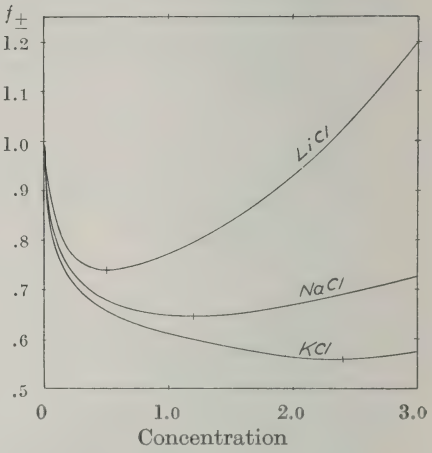


Fig. 2. Mean activity coefficients, $f_{\pm}$, experimentally determined in solutions of LiCl, NaCl, and KCl according to Getman and Daniels (1937).

$$-\log f_i = \frac{0.5 \cdot n_i^2 \cdot \sqrt{\mu}}{1 + A \cdot a \cdot \sqrt{\mu}}, \qquad (3)$$

where A signifies a constant which is dependent on the dielectric constant of the solvent and the temperature. a is equal to the sum of the radii of the hydrated cations and anions, but may even be regarded as the effective mean diameter of the ions, approximatively equal to the diameter of the ion + the »engere» hydration sphere. At low ionic strength values, appr. at $\mu < 0.01$, the denominator in formula (3) approaches the value 1, and formula (3) changes into (2).

The deviations from the formulas (1), (2) and (3) are individually different for the ions and, as a rule, increase rapidly at ionic strength values above 0.1.

For binary electrolytes the formula of Debye and Hückel gives the same activity coefficient for both the cation and the anion, but this is not always the case as is proved by the measurements of Hass and Jellinek (1932).

In figure 1, the relationship between $pf_{\pm}$, a and $\sqrt{c}$ is represented for some uni-uni-valent salts, whereby 0, 1, 2, 3, ... 8 Å have been

chosen as suitable a-values. The limit line $a = 0$ applies to ions conceived as charged points. At such an a-value, formula (3) changes into formula (2). The figure includes experimentally determined $pf_{\pm}$ values, taken from LANDOLT-BÖRNSTEIN's tables (1931), at different concentrations for the salts mentioned in the figure. It appears from figure 1 that with increasing concentration, the $pf_{\pm}$ curves deviate from the straight the faster, the higher the a-value, that is to say the greater the effective diameter of the ions is. Furthermore, the figure shows that the $pf_{\pm}$ values of the three salts LiCl, NaCl and KCl practically coincide at ionic strength values below 0.01 but, above this value, LiCl lies lowest, NaCl higher, and KCl highest. The differences between them grow in relation to the ionic strength and become considerable already at moderate ionic strength values. The Cl-ion being common for the salts mentioned, these conditions must be explained in the first place by the effect of the different size of the cation. As mentioned above, the volume of the hydrated ion decreases for these alkali cations in the order: Li > > Na > K. As a consequence, the a-value for the three alkali chlorides also decreases in the same order and, according to the theory, the relative position of the experimental values ought to be the same as the position of the calculated curves for the corresponding a-values at not too high ionic strength values. The figure, too, indicates that so is the case. Increasing a-values cause a decrease of the interionic forces. That, in its turn, leads to the consequence that, under otherwise identical conditions and at an ionic strength which is not too low, *the activity coefficient* for homovalent and chemically closely related ions *is the greater, the more hydrated the ion.* Thus, for the alkali ions, f increases in the order: Cs<Rb<K<Na<Li, cf. fig. 3. As will be seen from the experimental results, this relation is of fundamental importance for the interpretation of many ion exchange reactions.

Still, it is not always sufficient to consider the ionic diameter, when the activity coefficient is to be calculated at ionic strength values above 0.1. The deviations which occur may be caused, partly by a change of the dielectric constant of the solvent in the neighbourhood of the central ion — the ion swarm condenses when the concentration increases —, and partly by a beginning association between ions of opposite charge.

By theoretical considerations, BJERRUM (1926 a and b) arrived at the conception that, in certain cases, it might happen in electrolyte solutions that some of the ions are associated, that is to say the cations and anions are, on account of the interionic forces, so closely tied together in pairs that, outwards, they nearly behave as molecules. However, BJERRUM presumes that only Coulomb-forces are at work, so that an ion pair which is associated in such a way, must not be considered to be an undissociated molecule. The

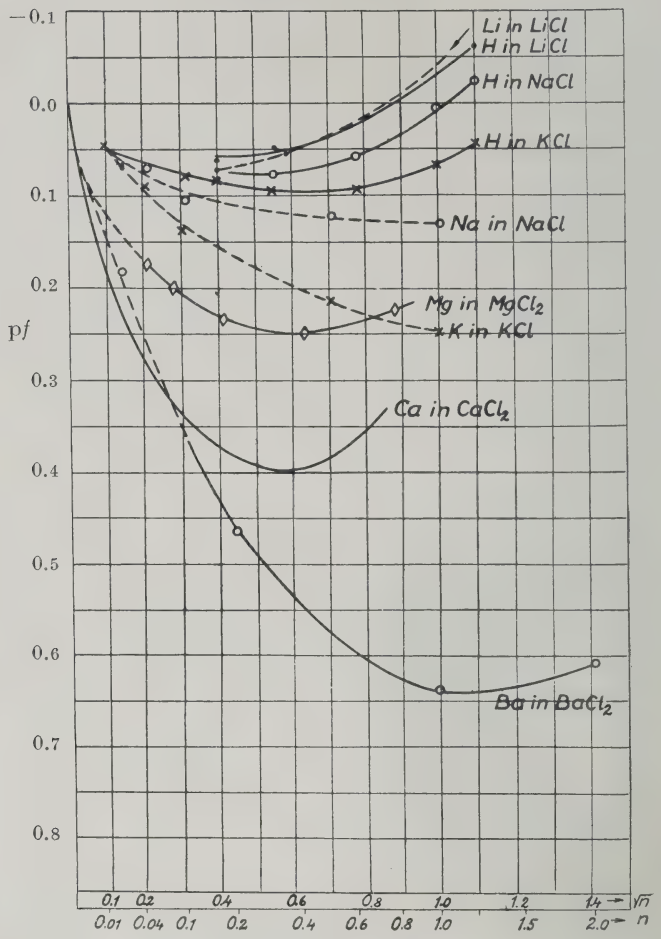


Fig. 3. Activity coefficients for Li, Na, K, Mg, Ca, and Ba, computed from $pf_{\pm}$ and pf_{Cl}, and f_H experimentally determined in alkali chlorides. Compiled from Du Rietz (1938).

equilibrium between associated and free ions is governed by the law of mass action whereby, however, activity is to be used. Association takes place when the distance between the charge centra of both ions falls below a certain minimum distance, r_m, which depends on the valence and the temperature and which can be represented by the following expression:

$$r_m = \frac{n_+ \cdot n_- \cdot \varepsilon^2}{2\,D\,k\,T},$$

where n denotes the valence, ε the unit charge, D the dielectric constant, k Boltzmann's constant, and T the absolute temperature. For monovalent ions in water at 18° C, r_m is equal to 3.52 Å. When the mean diameter, a, of a cation and an anion becomes less than r_m, ion association takes place to a greater or lesser extent. The degree of association increases rapidly with the increasing difference $r_m - a$ and with the concentration and valence of the ions. Ions of high valence and small ions are therefore, at not to low concentrations, associated to a considerable extent, while large, monovalent ions are not likely to show any noticeable association. Calculations made by BJERRUM (1926 a), MÜLLER (1927, 1928) and others showed that monovalent ions exhibit marked association effects only when $a < 2$ Å. Therefore, the alkaline chlorides, all of which have higher a-values than 2 Å, will not be associated. For bivalent ions the association already becomes noticeable when a falls below 7 Å; for this reason, the alkaline-earth chlorides probably show a tendency towards association at rather low concentrations. According to BJERRUM, $a = 5.8$ Å for $BaCl_2$.

As a consequence of ion association, the activity coefficient for the ions concerned is more or less reduced. When β indicates the degree of association, c the total ion concentration, and f_o the activity coefficient for the free ions, calculated according to DEBYE and HÜCKEL, the concentration of the free ions is equal to $c(1 - \beta)$, and the activity coefficient (f) for the electrolyte, when regarded as completely ionized, is determined by the expression:

$$f = f_o (1 - \beta).$$

Consequently, in solutions where $\beta > 0$, the formulas of DEBYE and HÜCKEL lead to too high values for the calculated activity coefficients as was shown by BJERRUM. MÜLLER (1927, 1928), GRONWALL, LAMER and SANDVED (1928) obtained similar results, though in a different way. The decrease of the activity coefficient through association, which takes place in the more concentrated solutions, is particularly noticeable in the case of the polyvalent ions.

There are divergent opinions as to what happens to the »sphere» of hydration water when the ions associate. When working out his association theory, BJERRUM presumed that only Coulomb-forces were at work; this means that the ions do not touch each other directly but that the »spheres» of chemically bound hydration water remain intact. ULICH (1933) mentions several reasons supporting this opinion. PAULI and VALKÓ (1929), on the other hand, maintain that in colloids the adsorption of strongly bound or associated counter-ions causes a partial or even complete dehydration at the point of contact. DU RIETZ (1938), too, supposes that the hydration water is not bound so strongly.

In the associated ion pairs the ions, according to BJERRUM, are supposed to retain their individuality. When ion association is connected with dehydration, the ion pair might be considered as either forming an intermediate stage between an ion pair, which is associated according to BJERRUM, and an undissociated molecule or, in certain cases, being actually identical with the latter. When the ions come into immediate touch with one another, it must be presumed that they become more or less deformed by polarization; this leads to a strengthening of the association and an increase in the degree of association. Nothing, however, is changed by this as to the principle.

The association conditions in colloids will be treated in a later chapter.

4. The Structure of the Micelle.

A colloid particle with surrounding ion swarm is called *micelle* according to DUCLAUX (1907). It consists of two parts: 1) an inner, electrically charged part which is often called *colloid ion* (PAULI and VALKÓ 1929) or *macroion*. The colloid ion consists of a solid kernel, called *ultramicron* (WIEGNER 1925), and an electrically charged layer, the so-called inner layer, attached to the kernel. 2) an outer part consisting of the oppositely charged ion swarm, the so-called *counter-ions* surrounding and electrically compensating the colloid ion. The part of the micelle outside the colloid ion is usually called *inside solution* or *micellar solution* in contrast to the *free* or *outside solution*.

Several theories have been published aimed at explaining the electrical properties of the micelle. The oldest among them is the theory worked out by HELMHOLTZ (1879) about the electrical double layer. The micelle is thought to act as an electrical condenser. The inner layer is formed by electrically charged groups or adsorbed ions on the outside of the ultramicron and this is surrounded by an outer layer of ions of opposite charge at short distance. HELMHOLTZ assumed that the thickness of the double layer was constant and of molecular dimension. However, the double layer of HELMHOLTZ gradually proved to be too schematic.

The theory advanced by GOUY (1910) was considered to mark an important progress. In conformity with HELMHOLTZ, he regards the inner layer as a uniform distribution of electrical charges on the surface of the ultramicron, whereas the outer layer is diffusedly distributed, forming an ion swarm. The density of the counter-ions is greatest next to the surface of the colloid ion and decreases continuously towards the outside solution. Also ions of the same charge as the colloid ion form part of the ion swarm, »*Nebenionen*» (PAULI

and VALKÓ 1929), which belong to the free electrolyte. The density of the nebenions increases towards the outside solution.

STERN's (1924) conception of the micelle structure includes both the double layer of HELMHOLTZ and GOUY's diffuse ion swarm. Innermost, the counter-ions form a densely closed one-ionic layer at the outside of which the other ions are diffusedly distributed with the density decreasing in the outward direction. In dilute solutions, STERN's double layer changes into GOUY's ion swarm, while, in concentrated solutions, it tends to change into the double layer of HELMHOLTZ.

It must be assumed that the ions forming part of the micellar solution but not being associated are freely mobile under the influence of thermic motion and the electrostatic forces. In other words, they are in equilibrium both with the colloid ion and the outside solution. For this reason, it is impossible to attribute some of the counter-ions to a salt emanating from the outside solution and others to the colloid ion. As a consequence of the electrostatic attraction, the concentration of the micellar solution is greatest at the surface of the colloid ion decreasing in the outward direction. In the outside solution the concentration is constant.

At first, the colloid ion was considered to be compact and more or less spherically shaped; furthermore, it was thought to be provided with a great number of charges attached rather regularly to the surface. However, this conception had to be abandoned as being too schematical as far as many ion exchanging substances were concerned.

By exchange reactions carried out by Wiegner and collaborators (CERNESCU 1933, WIEGNER 1936), by X-ray analysis of clay minerals, and by calculations of exchange capacity and charge density made by MATTSON (1926) and DU RIETZ (1938), it has been shown that the surface of solid ion exchangers is, as a rule, not even but more or less irregular, which leads to an augmentation of the surface. If this were not the case, the charge density of many ion exchangers would reach absurdly high values. The explanation might be found in a very high value for the specific surface, which is thought to arise in the following way:

The colloid particles may be either primary, monons, or secondary ones, polyons. In the latter case, they have originated from the aggregation of monons. Hereby no compact association occurs but plenty of channels, cavities and hollows of varying dimensions and shapes are formed. This is described by the expression that the ultramicron has inner and outer surfaces. It is internally dispersed.

Even the specific surface of the primary particles may be increased by irregularities in the crystal fracture or in the wall of the particles; these conditions are called metatexturation by WO. OSTWALD (1935). Moreover, certain substances have a crystal lattice which

is open to such an extent that ionic exchange can take place inside the lattice; such is the case e.g. with the montmorillonite and beidellite minerals. The inner surface of such ion exchangers naturally becomes very great. Certain organic ion exchangers of aromatic character are built in a net-like way, which leads to a very great specific »surface» and brings about ionic exchange inside the body. Ion exchangers of this type are the synthetic resins which will be dealt with in detail in part IV.

Du Rietz (1938) maintains the opinion that the colloid particles are of a gel-like nature. It might be assumed that such a conception could be specially applied to undried, isoelectrically precipitated silicates which have not had time to become crystalline.

As a matter of fact, there scarcely seems to be a distinctive difference between the gel hypothesis by Du Rietz when applied to permutite, and the conception about inner and outer surfaces. In many ion exchangers, e.g. permutite, the ultramicron undoubtedly forms a net-work of channels and cavities, on the metatextured walls of which the active ion exchanging groups are situated. Here, it is equally justified to speak about a gel as about a body with inner and outer surfaces. The behaviour of permutite in electrodialysis indicates that it is built in such a sponge-like way. When the permutite material used in the present investigation was electrodialysed, a so-called Mattson-cell was used (Mattson 1926). It could be observed that, when the material was not stirred up, the power of the current soon decreased to a low value but rapidly increased again, when stirring took place. Gradually the power of the current decreased again and anew increased after stirring. The power of the current showed the same development when the anode- and the cathode-poles were interchanged after the anode- and cathode chambers had been emptied and washed clean from electrolytes. The explanation might be found in the fact that the ions within many of the cavities and pores, in their migration towards the anode- or cathode-poles, have free passage only in one direction but are blocked up in the opposite direction. As soon as the unblocked ions have been removed, the power of the current decreases. Only after stirring up the permutite or exchanging the polarity, new pores can be emptied of their ion contents.

From the preceding discussions the conclusion may be drawn that ionic exchange to a great extent will be influenced by the structure of the colloid ion; as a matter of fact, this has been shown by Wiegner and collaborators (Wiegner 1936). When the exchange takes place on a monon which toward the reacting ions behaves as compact and which lacks inner surfaces, the process is, according to Wiegner, said to proceed in an »extramicellar» way.[1]

[1] The expression being inaccurate from the linguistic point of view, it will be replaced here by the expression *outer-surface ion exchange.*

The same applies for polyons when the structure is so fine that the reacting ions are unable to penetrate into the cavities. The »intramicellar» ionic exchange[1] (according to WIEGNER) takes place in the cavities of the polyon or within the crystal lattice of the monon, when the structure is sufficiently open.

Kaolinite may be mentioned as an example of materials with outer-surface ion exchange and low exchange capacity. In contrast to kaolinite montmorillonite shows inner-surface ion exchange and high ion exchange capacity. The explanation is to be found in the crystal structure of the mineral. For particulars see the following chapter.

According to its hetero-dispersed structure, permutite performs both outer- and inner-surface ion exchange and, for this reason, possesses high cation exchange capacity. While small ions have access to a great part of the ion exchanging surface, the larger ions, on account of their size, have to content themselves with a minor part; this condition is called *ion blockade* by WIEGNER (1936). The ion blockade increases with the size of the ions. The inner surface of permutite is very great in comparison with the outer surface; this is proved by the fact that no increase of the exchange capacity can be brought about by grinding the permutite, as was demonstrated by KELLEY and JENNY (1936).

5. The Crystalline Structure of Clay Minerals.

Ever since HADDING (1923) with the aid of X-ray analysis could demonstrate the occurrence of the minerals quartz, kaolinite and muscovite in the finest sedimentation products of clays and ROSS (1927) showed that crystalline clay minerals are universally present in soils, much interest has been devoted by crystallographically minded pedologists and geologists to studies of the clay fraction. By using X-ray analysis, the electron microscope, and thermal methods, attempts have been made to identify the clay minerals and to explain their crystalline structure, as well as to interpret, with the aid of the results thus gained, many of the chemical and physical properties of the so-called soil complex.

Most scientists within this sphere now seem to agree that, setting aside small possible amounts of quartz and felspars, clay colloids principally consist of crystalline silicates of the layer lattice type belonging to the mineral groups of montmorillonite, kaolinite, and mica (GRIM 1942, SCHACHTSCHABEL 1943). Besides montmorillonite, there are several minerals belonging to the montmorillonite group, as e.g. the rather common nontronite and beidellite — the latter being of a much disputed character — and the less frequently found

[1] Here called *inner-surface ion exchange.*

saponite. Even the kaolinite group comprises several minerals, the most common of which are kaolinite, halloysite and metahalloysite. The mica group — called illite group by Grim, Bray and Bradley (1937) — contains several minerals which are like white mica, but have lower potassium and higher water contents than this. The composition of montmorillonite may be described by the formula $Al_2O_3 \cdot 4SiO_2 \cdot H_2O + nH_2O$, beidellite by $Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$, nontronite by $Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O$ and kaolinite by $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

With regard to the crystal structure of the clay minerals, it can be stated that the results reached by the scientists, though certainly agreeing in general, often show rather grave differences, as far as the details are concerned which sometimes might be considered decisive for the properties of the mineral in question. In fig. 4 the structure of the most common minerals is shown.

These minerals have that in common that they are built from elementary layers which consist of one or two Si-O-tetrahedron planes and one Al-O-OH-oktahedron plane. A short description will be given here of how they, on account of their X-ray spectra, are thought to be built.

According to Hofmann, Endell and Wilm (1934) and Edelman and Favejee (1940), montmorillonite consists of elementary layers arranged side by side. Every elementary layer contains two Si-planes and between them one Al-plane. The Si-planes are built in such a way that the Si-ions, according to Hofmann et al. (1934) form the centre in an O-ion tetrahedron, while, according to Edelman and Favejee (1940), they form the centre in an O-OH-ion tetrahedron, figure 4. In the Al-plane the Al-ions are octahedrally surrounded by six O- and OH-ions. The tetrahedron and octahedron planes are kept together by mutual O-ions. The OH-groups bound to the Si-ions are likely to be able to give off protons and exchange cations. While the thickness of the elementary layer is constant, about 9 Å, the distance between two elementary layers can vary considerably. While the lattice forces within the elementary layer strongly bind the ions inside, the forces which are at work between the elementary layers are weak and therefore allow the layers to separate from each other under certain conditions. This, for instance, is the case when montmorillonite takes up water and swells. The water molecules penetrate between the elementary layers, whereby a one-dimensional swelling takes place which is directed rectangularly to the basal plane. On account of the great distance between the elementary layers in swelled up montmorillonite, the ions can easily migrate into the lattice. An inner-surface ion exchange takes place and, accordingly, the montmorillonite does not exhibit any ion blockade as has been demonstrated by Cernescu (1933) and Wiegner (1936). When saturated with sodium, montmorillonite is able to swell to such an extent that the lattice completely dis-

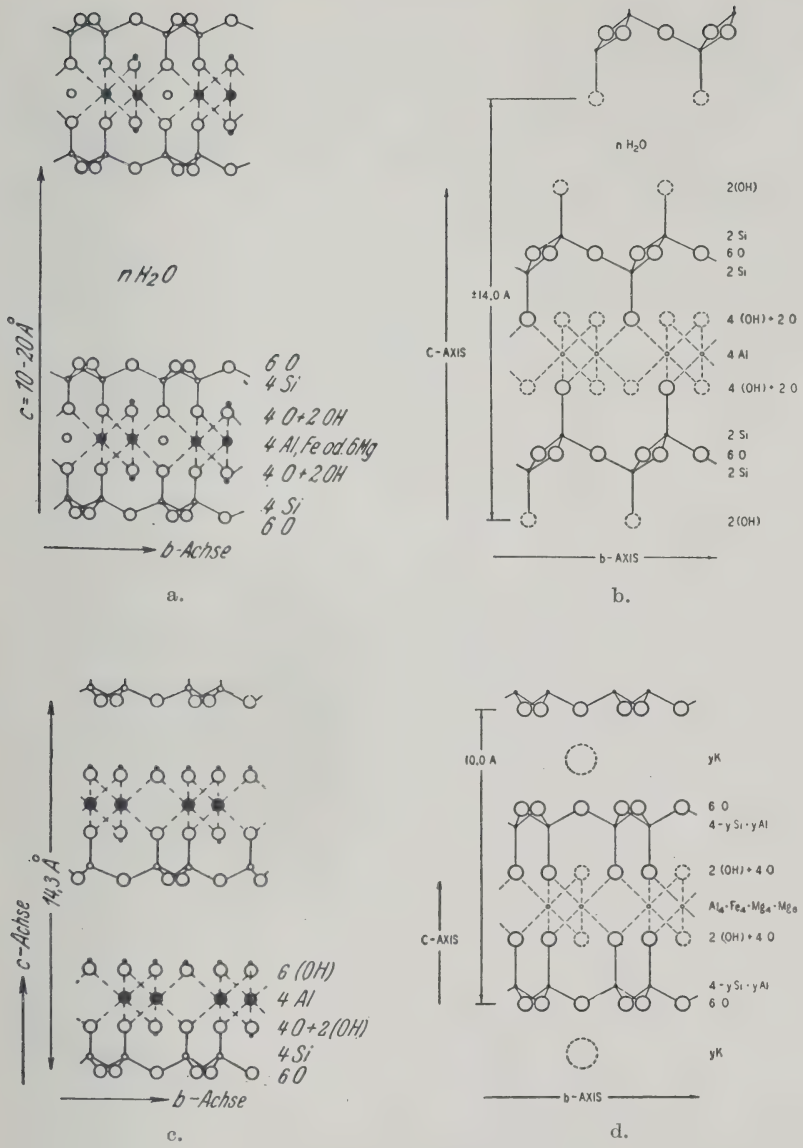


Fig. 4. Crystal structure in rectangular section to the lattice plane of:

a. montmorillonite, according to Hofmann, Endell and Wilm (1934);
b. montmorillonite, according to Edelman and Favejee (1940);
c. kaolinite, according to Gruner (1932);
d. illite, according to Grim, Bray and Bradley (1937).

integrates into elementary layers (Hofmann 1942). It is interesting to know that the density of the lattice in minerals of the montmorillonite-, beidellite- or nontronite-type is dependent, even in an air-dried state, on the type and the concentration of the saturating ion. Thus Gieseking (1939), on saturation with the large tributyl mono-heptyl ammonium ions, found considerably greater distances between the elementary layers than on saturation with smaller ions, as calcium or hydrogen.

According to Gruner (1932), kaolinite is built up from alternating planes of octahedral Al-O-groups and tetrahedral Si-O-groups, figure 4. The planes are mutually kept together by O-ions sitting between the Al- and Si-ions. Kaolinite has a very dense ion lattice which is considered to be responsible for the fact that only outer-surface ion exchange is to be found in kaolinite and that there is no ion blockade. The kaolinite group does not swell up in water.

The ground structure of the elementary layers in the mica-group is the same as in montmorillonite (Grim 1942) but the distances between the layers are small. As a further contrast to montmorillonite, the mica does not show any swelling in water (Hofmann and Giese 1939).

As a consequence of the composition and structure of montmorillonite and kaolinite, the former has a high ion exchange capacity, about 80—100 m.e./100 g, and the latter a low one, about 3—10 m.e./100 g. The mica-group occupies an intermediate position because ion exchange, according to Schachtschabel (1940), takes place both on the surface of the crystals and, to a certain extent, inside them. A detailed description of a great number of clay minerals with regard to their composition, structure and relationship is given in a monograph by Grim (1942).

It must be considered as proved that, as a rule, the clay colloids contain crystalline clay minerals as their main constituents. The inorganic ion exchange material in the soil which, a few years ago, was thought to consist mainly of amorphous aluminium and iron silicates of varying composition, is now considered by a great number of pedologists to consist of a few clay minerals which are well defined with regard to their structure. However, this opinion is not satisfactory from many points of view. The chemical decomposition constantly in progress in the soil which causes minerals to disintegrate and new ones to come into existence, thus creating soils of a marked variability even from identical parent material, naturally leads to the occurrence of transitionary forms of the different minerals. Soil is not a statical formation but must be considered as a complex system in which many different chemical and physical processes of constantly changing intensity are continuously going on, bringing about a dynamic state of the soil which never leads to real equilibrium.

Therefore, it was a matter of great interest, when MARSHALL (1935) by way of mathematical calculations could show that certain ions in the silicate lattice can isomorphously become replaced by others. Thus, MARSHALL found that in the silica tetrahedrons Si can be replaced by Al and to a minor extent by P, and in the aluminium octahedrons Al by Fe, Mg, and Ti. As a natural consequence of such a change in the composition of the silicate lattice, transition from one mineral to another is made possible, and the clay minerals can, without loosing their crystal structure, undergo modifications with regard to certain properties, as exchange capacity, isoelectric point etc. It is worth mentioning in this connection that LARSEN and STEIGER (1928) could prove the existence of a complete isomorphous series of transitional minerals between beidellite on one side and nontronite on the other.

Nothing is said about the velocity of this lattice ion exchange and about the influencing factors, but it may be assumed that the transformation proceeds very slowly and that it is intimately connected with the composition of the soil solution and with the weathering processes which, continuously in progress, are regulated by the different pedogenic factors. The ions in the lattice are tied together by the very strong lattice forces; for this reason, a change or decomposition of the lattice will be a very slow process. This exchange of lattice ions must not be mistaken for the process which usually is called ion exchange and which consists in an equivalent interchange of counter-ions in the ion swarm with ions of the same sign of charge in the outside solution. This ion exchange is an instantaneously accomplished reaction. A strict limit can hardly be drawn between lattice ion exchange and ordinary ion exchange. Judging by the results of HOAGLAND and MARTIN (1933), BRAY and DETURK (1938), and DETURK, WOOD, and BRAY (1943), it rather looks as if there existed an equilibrium between the lattice bound, »non-replaceable», and the easily replaceable ions. Whenever the expression »ion exchange» is used in the following, it is always intended to signify the exchange of counter-ions, if the contrary is not explicitly indicated.

KELLEY and JENNY (1936) have come to the conception that the minerals forming the clay fraction embrace a complex series of isomorphous minerals and that they are dependent with regard to both quality and quantity on the conditions prevailing in the soil. A corresponding view is expressed by JACOB (1942, 1943). With the aid of X-ray spectography and the electron microscope, JACOB and coworkers have been able to demonstrate that in the finer clay fractions, the clay minerals showed transitional states between the minerals which are typical for the coarser clay fractions. These conditions became the more marked, the more the diameter of the particles decreased. Thus, the clay minerals are not limited to a

small number of characteristic minerals, but are continuously subjected to disintegration and formation under the influence of the conditions in the soil.

To a great extent, this conception reconciles the opinion that the clay colloids represent distinct and statical, crystalline minerals, with the theory advanced by MATTSON (MATTSON and GUSTAFSSON 1937) and contested by some crystallographically working pedologists, about the gel-like soil complex as being the active part in the soil, which is dynamic as regards composition and dependent on the pedogenic factors. The correctness of MATTSON's opinion is underlined by the fact that HOFMANN (1942) found the bulk of the clay material in certain soils to consist of amorphous silicates.

Sometimes, the opinion is advanced that all inorganic ion exchangers are crystalline. Therefore, amorphous matter should not be able to perform ion exchange. Such a view must be rejected as being obviously wrong. Several technically used synthetic ion exchangers which are characterized by high exchange capacity, as Na-permutite, Filtrol etc., must be qualified as amorphous according to HOFMANN (1942). The same applies most probably to isoelectrically precipitated, not aged gels of iron and aluminium silicates as indicated by RINNE's (1924) investigations. RINNE subjected aluminium silicate, which had been precipitated by STREMME and kept for fifteen years, to X-ray analysis and verified herewith that the silicate gel was still amorphous. Even synthetic Na- and Mn-permutites were found to be amorphous. Further MATTSON (1938) increased the exchange capacity of Wyoming bentonite from 101 to 234 m.e./100 g by fusion with Na_2CO_3.

The crystalline state is the most stable one, and for this reason matter tends to pass from an amorphous into a crystalline state. But as a rule, the crystallization processes require a certain time. When iron and aluminium silicates are isoelectrically precipitated, the precipitation process is instantaneously accomplished. Therefore, it is difficult to imagine how any noticeable formation of crystals could have time to take place. Gels which have been produced in this way possess such a high cation exchange capacity that the greater part of this capacity must be ascribed to the amorphous gel, even if nontraceable microcrystals should have been formed. In consequence, only the acidoid theory is fitted to explain the base exchange capacity in such substances. The same applies to HOFMANN's allophane clay.

6. The Chemical and Physical Nature of the Surface Complex.

When it is a question of satisfactorily explaining the exchange reactions taking place in an ion exchanger, great emphasis has to be attached to a simple and correct conception, not only of the

structure of the ultramicron, but, to the same extent, of the structure and nature of the active or ionogen part of the micelle. The theories as worked out by HELMHOLTZ, GOUY, STERN and others only considered the structure of the ionogen part in general, including certain physical properties but not its genesis and chemical nature. By examining in detail the structure, genesis and function of the ionogen part in natural ion exchangers, greater possibilities have been opened towards a better understanding of the complicated and varying reactions which take place on ionic exchange. Among the most important theories aimed at explaining these reactions may be mentioned the *adsorption theory* and the *acidoid theory*.

The adsorption theory, which has had many supporters, at first considered the ionogen part as being something like the double layer of HELMHOLTZ (JENNY 1927). Later, in accordance with GOUY and others, the counter-ions were thought to be more diffusedly distributed (WIEGNER and PALLMANN 1929). The inner coating consists of OH-ions which are adsorbed on the surface of the ultramicron.

For many scientists, however, the adsorption theory appeared unsatisfactory from many points of view; for this reason, the whole problem was reconsidered under a more chemical aspect. In this way, the acidoid theory has been developed which, functionally, is of a much more universal character.

Here, attention shall be paid in the first place to those exchangers which are of greatest importance in pedology, the inorganic-organic soil colloids or soil complex.

In the latitudes of Sweden, the soil colloids are usually negatively charged and act as polyvalent insoluble acids, acidoids, because they protolyse hydrogen ions which are replaceable by added cations. But the soil colloids show even properties indicating that they have basic character, since they bind anions and at the same time set free OH-ions. They behave as basoids. On account of their acidoid and basoid properties, the soil colloids can be regarded as ampholytoids which form salts, saloids, with both bases and acids. Above the isoelectric point, I. E. P., the total charge as indicated by electrophoresis becomes negative, while it becomes positive below the I. E. P.

In most cases, the soil colloids seem to me to be a formation of:

1) a number of crystalline clay minerals forming the main mass of the clay particle, the silicate skeleton,

2) gel-like silicates of a more undefined character as to their composition,

3) humus matter.

The two latter components are found in intimate chemical and physical union with each other and with the surface of the silicate skeleton and form together with this the *surface complex* which is

the active part of the clay particle. The relative part played by the three components varies considerably from soil to soil and even a little with the seasons, the latter variation being dependent in the first place on the humus part.

The humus in the soil is likely to be more or less intimately bound to the lattice and gel-like mineral part, a view which is supported by Tyulin (1938).

Concerning the genesis of the ion exchanging properties of the soil colloidal material, there still seems to be some unclearness. It is most probable that OH-groups which are attached to the free surfaces of the lattice and are bound to Si-ions, behave like acids, and give off protons and exchange cations. The mineral reacts the same way as silicic acid with the exception that the active OH-groups are attached to a macroanion. The strongly acid suspension effect of electrodialysed bentonite, consisting mainly of montmorillonite, points to the presence of protolysed H-ions and consequently indicates acidoidic nature. There are other inorganic ion exchanging substances showing the suspension effect increasing in proportion to the strength of the acidoid. The good correlation existing between the ion exchange capacity and the specific surface of the minerals, which has been undisputably shown by Kelley and Jenny (1936), proves that ion exchange can take place on the lattice surfaces of the minerals and, presumably, in the way mentioned above. The authors have succeeded in raising the base exchange capacity up to several hundred per cent by grinding some minerals and soil colloids.

It has been postulated by Hofmann, Endell and Wilm (1934) that in the clay minerals the exchangeable ions are held fast by what might be called »broken bonds». The breaking up of the clay crystal results in a breach between Si-O-Si in the silica tetrahedron layer and thereby in free bonds. According to the aforesaid investigators, these bonds are compensated in such a way that cations are bound, whereafter they become capable to act as exchangeable ions in water. No detailed explanation is given as to how the reaction is accomplished. Thus, the low cation exchange capacity of kaolinite is explained by the fact that the exchange is confined to broken bonds (Grim 1942).

However, such a conception of the origin of the ion exchange is impossible because the electro-neutrality must be maintained both in the crystal and in its environment. In contrast, the reaction is likely to take place under participation of water molecules. In connection with the breaking of the crystal, breaches can arise both in the Si-O-Si and in the Si-O-Al bonds. With every splitting of this kind one negative and one positive bond are set free and, therefore, one H-ion and one OH-ion from the water can take part in the reaction in the following way:

$$\text{Si-O-Si} + \overset{+}{\text{H}} + \overset{-}{\text{OH}} = \text{Si-OH} + \text{Si-OH}$$

$$\text{Si-O-Al} + \overset{+}{\text{H}} + \overset{-}{\text{OH}} = \text{Si-OH} + \text{Al-OH}$$

In the crystal breach, OH-groups arise which are able to act as acid (Si-OH) and base (Al-OH) respectively.

It seems to be rather unlikely that, as KELLEY et al. (1936) assume, the broken bonds should polarize and adsorb water-molecules, »broken-bond-water», which thereafter would give off H-ions. By this, the »broken bonds» cannot get neutralized as, on the contrary, is the case if the reaction takes place as mentioned.

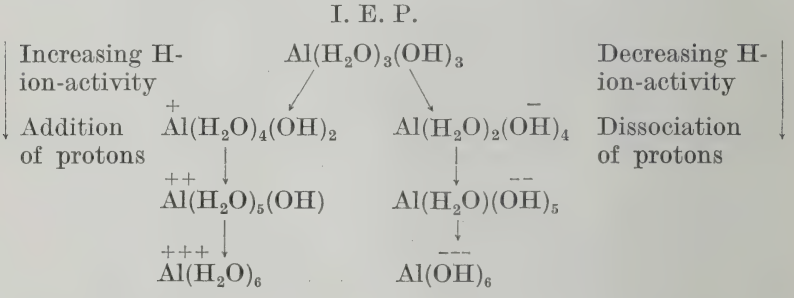
HENDRICKS (1942) and others apparently intend to explain the base exchange capacity of the montmorillonite-like minerals as being mainly dependent on substitutions in the lattice, Mg^{2+} for Al^{3+} and Al^{3+} for Si^{4+}, resulting in the formation of free negative charges (from uncompensated oxygen ions) which become compensated by the exchangeable cations. But even in this case, the cation exchange is naturally localized to OH-groups acting as acids. Such a lattice substitution certainly plays an important rôle in the origin of the base exchange capacity in these minerals with their small particles and open lattice structure, but it can be reasonably doubted if the lattice substitution is alone responsible for the ion exchange capacity, as should be the case if the lattice was built according to HOFMANN, ENDELL and WILM (1934). In consequence, a not substituted montmorillonite of this structure should have an exchange capacity approaching zero. EDELMAN and FAVEJEE (1940) avoided this difficulty by assuming Si-bound OH-groups to be attached to the surfaces of the elementary layers, fig. 4. The OH-groups bound to the Al-octahedrons, which moreover are placed inside the elementary layer-lattice, are hardly able to release H-ions and to bind cations to a larger extent at the pH values which generally prevail in the soil.

However, the views mentioned above are insufficient to explain the exchange conditions in the soil colloids in general and especially in the amorphous ion exchangers. As emphasized before, the soil colloids consist not only of a regular lattice but have a more complex structure. Anyhow, taking the theory of DAMSGAARD-SØRENSEN (1941) as a basis and with reference to the above postulated composition of the soil complex, it is still possible to get a reasonable picture of the surface complex from the conception of a crystal lattice forming the bulk of the exchange complex.

Apart from OH-groups tetrahedrally bound to Si and functioning as acids, one could imagine that charged groups or ions originating on the lattice are attached to the inner and outer crystal surfaces of the ultramicron by means of oxygen atoms. These ions or groups

are of a varying nature according to the colloid character. In soil colloids which are built mainly from SiO_2, Al_2O_3, Fe_2O_3, MO, M_2O and humus, the ionogen part principally consists of aluminiumaquo [—$Al(H_2O)_3(OH)_2$], ferriaquo [—$Fe(H_2O)_3(OH)_2$] and silicic acid groups [—$Si_xO_y(OH)_z$] which are mosaically distributed and tied to Al- and Si-ions in the lattice by oxygen atoms. Even carboxyl (—COOH) and phenol groups (—C_6H_4OH) belonging to the humus component form an important part of the surface complex. As far as phosphoric acid is found in the complex, it too will contribute to the charge of the colloid. Other inorganic colloids as permutite, Fe-silicate and Al- and Fe-phosphate can be thought to be built in an analogous way as far as the active groups are concerned.

$Al(H_2O)_3(OH)_3$ reacts amphoterically. Below the isoelectric point it behaves as a weak base thus binding protons in an ever increasing degree and becoming more and more positively charged, the more acid the solution is. Above the isoelectric point, it reacts as a weak acid giving off protons and becoming negatively charged. These relations can be illustrated in the following way:



The [—$Al(H_2O)_3(OH)_2$]-group which is bound to the lattice will consequently react as either base or acid in accordance with the H-ion concentration in the outside solution. As the group is written here, it can be said to be in its isoelectric condition. The positive charge is neutralized by the O-ion forming the bond to the lattice. Below the I. E. P. the group takes up protons thus getting a positive charge and binding anions. Above the I. E. P., on the other hand, the group will dissociate protons, become negatively charged and bind cations. The following schematical formulas[1] may illustrate the development at addition of hydrochloric acid:

$$—Al(H_2O)_3(OH)_2 + \overset{+}{H} + \overset{-}{Cl} = —\overset{+}{Al}(H_2O)_4\,OH \,\vdots\, \overset{-}{Cl}$$

$$—\overset{+}{Al}(H_2O)_4OH \,\vdots\, \overset{-}{Cl} + \overset{+}{H} + \overset{-}{Cl} = —\overset{++}{Al}(H_2O)_5 \,\vdots\, 2\,\overset{-}{Cl}$$

[1] In the formulas, $\vdots$ indicates the limit between colloid ion and counter-ion.

When more acid is added, the group binds a third proton but becomes hereby detached from the lattice and goes into solution as $Al(H_2O)_6Cl_3$. Herewith the disintegration and dissolution of the lattice is initiated.

If sodium hydroxide is added, the corresponding equation will become:

$$—Al(H_2O)_3(OH)_2 + \overset{+}{Na} + \overset{-}{OH} = —Al(H_2O)_2(\overset{-}{OH})_3 \,\vdots\, \overset{+}{Na} + H_2O$$

$—Fe(H_2O)_3(OH)_2$ reacts in a similar way but its isoelectric point is somewhat lower than that of the Al-group.

The protolysis of the silicic acid-, the phosphoric acid- and the humic acid-groups is also regulated by the hydrogen ion activity. In contrast to the Al- and Fe-groups, these acidoid groups possess only acid properties and, in general, are alone responsible for the cation binding capacity of the soil colloids and for the acid reaction which the colloids show in an unsaturated state. The cation binding capacity that can be ascribed to the Al- and Fe-groups, is of a merely theoretical interest in connection with normal soils under Swedish conditions, because the isoelectric point for these groups lies so high that cation binding on a larger scale is scarcely possible. On lateritic soils the cation binding of these amphoteric groups might be of importance since the pH of the soil is often high and the complex is rich in sesquioxides.

The acid binding capacity of the soil colloids has to be ascribed in the first place to the basoid Al- and Fe-groups and, to a certain extent, to $—NH_2$ belonging to the humus component.

The isoelectric point of the colloid complex is determined by the relative strength and quantitative amount of the acidoid and basoid parts. This has been experimentally demonstrated in several papers by Mattson (1930, 1931). The equi-ionic point — the pH value at which the H- and OH-ion saturated complex can bind equivalent quantities of cations and anions (Mattson and Wiklander 1937) — which is an important characteristic of the amphoteric properties of an ion exchanger, is also determined by the above mentioned factors.

7. The Strength of Acidoids and Basoids.

As appeared from the preceding chapter, the active groups of the soil colloids behave like weak acids and bases except that they are attached to the kernel of the colloid particle which forms a giant ion, macroion. It may even be said that the active groups are »solved» in the micellar solution but, on account of their attachment to the colloid kernel, they are not subjected to thermic motion beyond the Brownian movement of the colloid particle as a whole.

The protolysation of the acidoid groups may be assumed to be governed by the same laws which are valid for ordinary acids. Thus, the protolysation equilibrium is described by the expression:

$$\frac{[\overset{+}{H_3O}]\ [\overset{-}{A}]}{[HA]} = k_s,$$

where HA signifies the unprotolysed acidoid and $\overset{-}{A}$ the acidoid anion. In polyvalent groups protolysation proceeds in steps, as in common polyvalent acids, and with decreasing degree of protolysation. The hydrogen ions are solved in the micellar solution, the acidity of which will be determined by both the concentration (molarity), the valence of the acidoid groups, and the degree of protolysation.

The hydrogen-ion concentration may vary from point to point in one and the same ion exchanger depending on a physical and chemical heterogenity of the material. At one spot the acidoid groups may sit more densely than at another; this, especially, should be the case on inner surfaces, in furrows and cavities. Moreover, the acidoid groups may, according to their nature, vary considerably as to the degree of protolysation. The micellar solution will then be inhomogeneous. This surely applies to the soil colloids which possess groups with varying acidity, from the rather strong humus acids over the weak silicic acid to the very weak sesquioxides. The mutual position of the groups certainly influences their strength as is the case in organic acids according to Bjerrum (1923).

The hydrogen ion concentration in the micellar solution in different ion exchangers varies considerably as measured by the pH_u of their suspensions. Thus according to Marshall (1942) the H-ion activities of the electrodialysed clays are in the order: Montmorillonite>beidellite>illite>kaolinite. Samuelson (1944) was able to compute that an exchange resin, which was saturated with hydrogen, had a 2.7 N. micellar solution, while another was only 0.027—0.069 N. Both were completely protolysed, their main difference being that the sulphonic-acid-groups were sitting more densely in the former than in the latter. In H_2-saturated condition the mineral colloids of the soil must be assumed to possess a rather dilute micellar solution; as a matter of fact, they behave like weak acids at titration. The humus fraction of the soil probably has a somewhat higher acidity than the mineral fraction.

If all acidoid groups were equally strong, the acidoid would behave as a common acid and yield a neutralization curve of the same shape as an acid. Such is not the case in soil colloids for, there, one has to do with acidoids the acid groups of which have different valence and dissociation constants. Consequently, the neutralization curve is a compound curve representing a series of overlapping curves of the individual acid groups.

Puri and Asghar (1938) have made titration curves of soils and considering these as dibasic weak acids they have calculated the pk_1 and the equivalence point between pk_1 and pk_2. The authors do not give any theoretical explanation for their assumptions and calculations. Judging from the curves which they present, the determination of the equivalence point and, by that, of pk_1 must be considered to be somewhat arbitrary. Such a procedure rests on the supposition that the dissociation constants of those acid groups which correspond to the first stage of the (imagined) dibasic acid, are only slightly different, but that they differ considerably from the corresponding constants of the second protolysation stage. It must be considered extremely doubtful that this is generally the case.

The degree of protolysation in an acidoid depends, apart from the strength of the acidoid, to a great extent on the amount and the kind of the neutral salts present; this question will be treated further in part III.

The protolysation conditions of the basoids are much less known than those of the acidoids. As a rule, the basoids are weak; this applies in the first place to the basoids to be found in the soil. The protolysation of the Al and Fe groups has already been discussed. As in the acidoids, the protolysation of the basoids depends on the kind and the amount of the neutral salts present.

8. Neutralization Curves and Cation Exchange Capacity.

In acidoids and ampholytoids with slightly protolysed acidic groups the protolysation and, with that, the capacity to bind bases increases with the pH-value in the outside solution.

The course of the neutralization curve, its more or less steep ascent, is determined partly by the pk-values of the acidic groups, the intensity-factor, partly by the actual amount of these groups, the capacity-factor. Even the kind and quantity of present salts are important (Mattson and Wiklander 1940).

As the base or cation exchange capacity of an ion exchanger one generally designates the number of m.e. cations of a certain kind which 100 g of the exchanger are able to bind at the pH-value 7.00 in the salt-free outside solution. The exchange capacity varies for a certain ion exchanger in proportion to the replacing power of the saturating ion. For most of the ion exchangers the exchange capacity at pH 7 is not identical with the total exchange capacity. This is explained by the fact that the protolysation of the acidoid is not complete at this pH-value.

Where not otherwise stated, all determinations of the cation exchange capacity given in the following experimental parts refer to pH 7 and are calculated per 100 g H-saturated material dried in the vacuum above P_2O_5 at room temperature.

9. The Application of the Activity Concept to Colloids.

The activity concept has long been used successfully for common electrolytes, while its application to colloidal electrolytes for the interpretation of exchange reactions has been confined to a few papers during the last years.

When ionic exchange is studied, the activity factor of the individual ions and their variations according to the composition of the solution are of greatest interest, while the mean activity factors are of inferior importance. However, it has, so far, proved very difficult to obtain exact values for the activity factors of the individual ions; this applies particularly to the ions forming part of the ion swarm. The method proposed by MARSHALL and BERGMAN (1941) and MARSHALL (1942, 1944 a) seems to be particularly interesting and promising; according to this method the cation activity is determined electrometrically by using membranes consisting of clay mineral, e.g. montmorillonite and beidellite, in the same way as the glass electrode is used for determination of the hydrogen ion activity. The method is applicable even in colloidal systems; however, it must be assumed that the method cannot give true values of the activity in the micellar solution.

A dilute solution of a strong electrolyte contains no salt molecules but is a solution of ions. All reactions which eventually may occur, take place between the ions and not between molecules and, since activity is practically regarded as effective concentration, it should be more correct to use ion activity instead of the mean activity of the electrolytes. In spite of the fact that the ion activity concept is widely used by physicists and chemists, objections against its use have been raised by GUGGENHEIM (1929) and later by DAVIS (1942), who reject the ion activity because it cannot be thermodynamically defined and exactly determined by experiment. However, BRØNSTED et al. (1932) believe that ion activity, though being inapproachable by ordinary thermodynamical methods, nevertheless has a physical meaning, and DU RIETZ (1938) emphasizes the importance of ion activity to the studies of ionic exchange.

In this connection, it might also be of interest to quote MARSHALL's (1944 a) refutation of the objections against the ion activity concept: »There is, however, nothing in GUGGENHEIM's treatment which really bears on the question as to whether non-thermodynamic evidence may legitimately be combined with thermodynamic. We are surely entitled to do this if by so doing we can advance our total knowledge. All we have to bear in mind is that the result will not be *thermodynamically* well defined, but it is not necessarily any the worse for that.«

In a paper published recently, however, DAVIS (1945) seems to

have left his former position by now applying ionic activities in connection with discussions on base exchange equilibria.

The difficulty in calculations and conclusions encountered in the study of exchange reactions in colloids is due to the fact that, as a rule, their micellar solution is concentrated. In dilute systems it is possible to calculate the activity coefficient according to DEBYE-HÜCKEL-BJERRUM, but this is impossible in more concentrated systems. However, there is reason to believe that in such solutions the activity coefficient of an ion decreases with increasing ion strength and, on the whole, in about the same way as in dilute systems. This is confirmed by measurements and calculations carried out by HASS and JELLINEK (1932) and DU RIETZ (1938). At high concentrations, however, the activity coefficients may behave differently so far as they may increase again; these conditions will be dealt with more closely in another connection.

Setting aside all cases where the conditions might be complicated in the way just mentioned, the activity coefficient of an ion will always be lower in the micellar solution than in the outside solution because the ionic strength is greater in the former than in the latter. The ionic strength increases continuously from the outside solution towards the surface of the colloid ion; therefore, the activity coefficients of the ions decrease in the same direction. According to the formula of DEBYE and HÜCKEL the *f*-value will fall faster for a bivalent than for a monovalent ion and more rapidly for a trivalent than for a bivalent one. Moreover, the *f*-value decreases faster for a slightly than for a strongly hydrated ion; compare fig. 1. Thus the activity coefficients of the following ions are reduced in the order:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{La}.$$

Results gained by MARSHALL (1942) support such a conception. When determining the Ca- and K-ion activity in a 4–5 % Putnam clay suspension, MARSHALL found that the ratio between the activities of Ca and K was 0.15 when the molar ratio was 1.5. Consequently the activity of Ca was reduced ten times more than that of K.

The more dilute the outside solution, the greater is the ratio between the activity coefficients in the outside and inside solutions. At high outside concentrations a levelling of the ionic strength and, with this, of the activity coefficients takes place.

The activity coefficient of the adsorbed ions is determined in the first place by the ionic strength of the colloid ion in analogy to the fact that the *f*-value of a cation essentially is a function of the anion strength. When the charge density of the polyvalent colloid ion is great, the colloid ion strength becomes high and the value for the activity of the adsorbed ions low.

Since the surface of the colloid ion is not even (metatexturation

and innerdispersity), and the charging groups or ions are not always regularly distributed on the surface, the charge density may vary from one point to the other, so that the micellar solution becomes inhomogeneous. The activity coefficients of a certain ion may, therefore, vary from one point to another which, in its turn, may lead to variations in the replacing power.

The saloids have often been considered as incompletely dissociated salts. The strongly replacing ions, as Ca, Ba, Cu, Ag etc., were thought to form slightly dissociated compounds while e.g. the Na-saloids were strongly dissociated. Certain scientists, BJERRUM (1926 a), PAULI and VALKÓ (1929), PALLMANN (1930) believe, however, that, in spite of the nature of the colloids as weak acids or bases, their salts are completely dissociated exactly as the salts of ordinary electrolytes.

If, in accordance with BJERRUM, one supposes complete ionization of the saloids, it is probable that, on account of the high charge of the colloid ion, the BJERRUM ion association plays a still greater rôle for the colloids than for the common electrolytes. These conditions are reflected by a low activity coefficient and a great replacing power for ions showing association tendency. Also HARTLEY (1935) adopts the conception of association by saying: ». . . in order to account for experimental results, some kind of association between micelles and ions of opposite charge must occur.»

A quantitative treatment of the association in colloids has not yet been possible but, qualitatively, important conclusions may be drawn as to which factors will influence the degree of association. These are in the first place the charge density of the colloid ion as well as the valence and electrodynamic radius of the counter-ions. Increasing charge density and valence favour the association, while it is counteracted by increased radius. As mentioned before, PAULI and VALKÓ (1929) assume that on association a partial dehydration of both the colloid ion and the counter-ion takes place at the point of contact. This may lead to polarization of both ions and an increased association as well as to an increase in the replacing power. Consequently, the hydration counteracts the association while the polarizing power and the polarizability (the ability of becoming polarized) of the colloid- and the counter-ion favour it. Under otherwise equal conditions the association tendency for the alkaline ions ought to increase in the following order:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs}$$

and for the alkaline-earth ions:

$$\mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba},$$

because the hydration decreases and the polarizability increases in that direction.

10. The Donnan Equilibria.

The reaction taking place in connection with ion exchange between a H-saturated acidoid and a neutral salt, e.g. NaCl, may be described in the following way:

$$\overset{+}{H}_i + \overset{+}{Na}_o \rightleftarrows \overset{+}{H}_o + \overset{+}{Na}_i$$

H-ions in the inside solution are exchanged for Na-ions from the outside solution; this process goes on until a dynamic equilibrium has been reached. When the law of mass action is applied, the following formula results:

$$\frac{(\overset{+}{H})_o \cdot (\overset{+}{Na})_i}{(\overset{+}{H})_i \cdot (\overset{+}{Na})_o} = K$$

The corresponding reaction for a basoid is written as follows:

$$\overset{-}{OH}_i + \overset{-}{Cl}_o \rightleftarrows \overset{-}{OH}_o + \overset{-}{Cl}_i$$

$$\frac{(\overset{-}{OH})_o \cdot (\overset{-}{Cl})_i}{(\overset{-}{OH})_i \cdot (\overset{-}{Cl})_o} = K$$

i signifies the inside solution (micellar solution), *o* the outside solution and ( ) activity. The equilibrium in such a system may also be expressed by the so-called Donnan equation which shall be briefly dealt with.

The state of ion equilibrium in a colloidal system was formulated in 1911 by Donnan for ideal systems (Bolam 1932). In the course of his experimental investigations aimed at verifying the equilibrium law, Donnan showed the necessity to introduce activity instead of concentration, since no colloidal electrolytes can be considered ideal. A micelle forms a microsystem. The counter-ions are solved in the micellar solution but prevented by the electrostatical forces from diffusing into the outside solution; by this a Donnan distribution arises.

In words Donnan's equilibrium may be formulated as follows: The product of the ion activity of an electrolyte within a system is constant everywhere. Ions with higher valence than 1 must be inserted as a root expression corresponding to the valence.

In analogy herewith, the distribution of the ions within the micelle and between this and the outside solution may be expressed in the following way, when HCl, NaCl and $CaCl_2$ are chosen as free electrolytes:

$$(\overset{+}{H})_i \cdot (\overset{-}{Cl})_i = (\overset{+}{H})_o \cdot (\overset{-}{Cl})_o \tag{4}$$

$$(\overset{+}{Na})_i \cdot (\overset{-}{Cl})_i = (\overset{+}{Na})_o \cdot (\overset{-}{Cl})_o \tag{5}$$

$$\sqrt{(\overset{++}{Ca})_i} \cdot (\overset{-}{Cl})_i = \sqrt{(\overset{++}{Ca})_o} \cdot (\overset{-}{Cl})_o \tag{6}$$

A clearer and more general expression is obtained by dividing (4) by (5) and (5) by (6) and then combining the quotients:

$$\frac{(\overset{+}{H})_o}{(\overset{+}{H})_i} = \frac{(\overset{+}{Na})_o}{(\overset{+}{Na})_i} = \frac{\sqrt{(\overset{++}{Ca})_o}}{\sqrt{(\overset{++}{Ca})_i}} = \frac{\sqrt[3]{(\overset{+++}{La})_o}}{\sqrt[3]{(\overset{+++}{La})_i}} \tag{7}$$

When a trivalent ion takes part in the equilibrium, it is expressed in the formula by the cube-root of its activity etc. For basoids an analogous consideration leads to the corresponding formula:

$$\frac{(\overset{-}{OH})_o}{(\overset{-}{OH})_i} = \frac{(\overset{-}{Cl})_o}{(\overset{-}{Cl})_i} = \frac{\sqrt{(\overset{--}{SO_4})_o}}{\sqrt{(\overset{--}{SO_4})_i}} = \frac{\sqrt[3]{(\overset{---}{Fe(CN)_6})_o}}{\sqrt[3]{(\overset{---}{Fe(CN)_6})_i}} \tag{8}$$

When the ionic equilibrium in a micelle is expressed by the law of mass action as well as by the Donnan equilibrium, it ought to be possible to pass from the former into the latter expression. Compare the law of mass action with the formulas (7) and (8). Obviously, this is only possible, if $K = 1$. By deriving kinetically the law of mass action for the ion exchange process, however, it is possible to show that K must have the value 1.

It is often suitable to distinguish in the Donnan equilibrium between the ions emanating from the colloid and the free salt in the micellar solution; then the following formula is obtained:

$$\frac{x_H}{y_H + z_H} = \frac{x_{Na}}{y_{Na} + z_{Na}} = \frac{\sqrt{x_{Ca}}}{\sqrt{y_{Ca} + z_{Ca}}}, \tag{9}$$

where x signifies the activity of the ion in the outside solution, y the activity of the same ion belonging to the free salt in the micellar solution and z the activity in the micellar solution of the ion dissociated from the acidoid. $y_H + z_H$, thus, are equal to $(H)_i$. An analogous expression is valid for basoids.

Attention, however, must be paid to the fact that only the free protolysed H- and OH-ions directly take part in the equilibrium

but not the total protolysable amount. With regard to the weak acids, HANTZSCH (1923) has advanced the hypothesis that they mainly consist of unprotolysable pseudo-acids which by a structural transformation may pass into genuine and protolysable acids.

In contrast, the aciform is dominating in strong acids. In the pseudoacids the hydrogen atom is bound homopolarly, while it is bound heteropolarly in the aciform thus becoming protolysable. Analogous conditions may prevail in acidoids. A low degree of protolysation leads to low activity, so that only a low H-ion concentration in the outside solution is required for the maintenance of the equilibrium.

When cations other than H-ions are present, they influence the degree of protolysation of the acidoid. They reduce the activity of the acidoid ion and replace some free H-ions causing the protolysation, which is ruled by the law of mass action, to continue until equilibrium is reached anew. The strength of the acidoid seems to increase, as is indicated by the fact that the dissociation constant appears to grow. It may be concluded from what was said before that this effect will be the greater, the stronger the replacing power and association tendency of the cation.

For an ampholytoid both formulas (7) and (8) must be valid at the same time.

When the constant ion product and the variation of the activity coefficients of the ions in relation to the ionic strength are known, it is possible to draw some important qualitative conclusions as to the ion equilibrium in acidoids in which all exchanging groups are accessible to the ions:

1. When an ion passes from the outside solution into the inside solution, its activity coefficient is reduced. As mentioned in the preceding chapter this reduction may be described by the following relative order:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{La}.$$

It follows from the law of the constant ion product that, if the equilibrium shall be maintained, the *concentration* of a certain ion in the micellar solution must be the greater in comparison with that in the outside solution, the stronger the reduction of its activity coefficient. This becomes evident when the concentration and the f-values of the ions are inserted into the Donnan equilibrium. NaCl is chosen as electrolyte.

$$(f_{\mathrm{Na}} \cdot c_{\mathrm{Na}} \cdot f_{\mathrm{Cl}} \cdot c_{\mathrm{Cl}})_i = (f_{\mathrm{Na}} \cdot c_{\mathrm{Na}} \cdot f_{\mathrm{Cl}} \cdot c_{\mathrm{Cl}})_o .$$

At equal activity in the outside solution, the concentration in the micellar solution and, by this, the replacing power will therefore lie in the order:

$$Li < Na < K < Mg < Ca < Sr < Ba < La,$$

the order being in agreement with the lyotropic series.

At very high concentrations in the inside solution, deviations from this order may occur on account of the »abnormal» variation of the activity coefficients. As long as there are no structural impediments of the ion exchange and no specific reactions, as lattice ion exchange etc., occur, the replacing power of an ion is the greater, the lower its activity coefficient in the inside solution, and the mutual order coincides with that given above; this becomes evident when the Donnan-equation is written in the following way:

$$\frac{f_{Na_o} \cdot c_{Na_o}}{f_{Na_i} \cdot c_{Na_i}} = \frac{f_{K_o} \cdot c_{K_o}}{f_{K_i} \cdot c_{K_i}}$$

2. Homovalent ions, the activity coefficients of which vary in the same way with the ionic strength, replace just as strongly, and their relative concentrations in the outside solution indicate at the same time their relative concentrations in the inside solution. This holds true even when the micellar solution is not homogeneous.

3. In paragraphs 1. and 2. the equilibrium conditions of ions with equal valence have been treated. If, on the other hand, one has to do with ions of different valence, not only the activity coefficients are to be considered but also the relative activities of the micellar and outside solutions. When the outside activity is low and the inside activity high, a bivalent ion will have a stronger replacing effect than a monovalent one, because the square root relationship is considered and the f-value of the divalent ion in the micellar solution is lower. This so-called valence-effect is the more marked, the greater the ratio between the activities of the inside and outside solutions. The latter approaching zero the valence-effect asymptotically turns towards a maximum. A near equalization of the inside and outside activities, on the other hand, leads to the consequence that the valence-effect tends to disappear; at increasing outside concentration the monovalent and bivalent ions gradually become more and more equal from the point of view of replacement. This may best be illustrated by the following simple calculations. The activity of both KCl and $CaCl_2$ in the outside solution is assumed to be in case 1) 0.0001 N., in case 2) 0.01 N. and in case 3) 0.5 N.; in the inside solution the activity of K is assumed to be in case 1) 0.01 N., in case 2) 0.1 N. and in case 3) 0.6 N. The activity of Ca in the inside solution, the ratio between the inside and outside activity, and the ratio $(Ca)_i : (K)_i$ are calculated with the aid of the Donnan equation:

$$(K)_o : (K)_i = \sqrt{(Ca)_o} : \sqrt{(Ca)_i}$$

1) $$\frac{0.0001}{0.01} = \frac{\sqrt{0.0001}}{\sqrt{(\mathrm{Ca})_i}};$$

$$(\mathrm{Ca})_i = 1;\ \frac{(\mathrm{Ca})_i + (\mathrm{K})_i}{(\mathrm{Ca})_o + (\mathrm{K})_o} = 5020;\ \frac{(\mathrm{Ca})_i}{(\mathrm{K})_i} = \frac{1}{0.01} = 100.$$

2) $$\frac{0.01}{0.1} = \frac{\sqrt{0.01}}{\sqrt{(\mathrm{Ca})_i}};$$

$$(\mathrm{Ca})_i = 1;\ \frac{(\mathrm{Ca})_i + (\mathrm{K})_i}{(\mathrm{Ca})_o + (\mathrm{K})_o} = 55;\ \frac{(\mathrm{Ca})_i}{(\mathrm{K})_i} = \frac{1}{0.1} = 10.$$

3) $$\frac{0.5}{0.6} = \frac{\sqrt{0.5}}{\sqrt{(\mathrm{Ca})_i}};$$

$$(\mathrm{Ca})_i = 0.72;\ \frac{(\mathrm{Ca})_i + (\mathrm{K})_i}{(\mathrm{Ca})_o + (\mathrm{K})_o} = 1.32;\ \frac{(\mathrm{Ca})_i}{(\mathrm{K})_i} = \frac{0.72}{0.60} = 1.2.$$

While the ratio between the sum of the calcium and potassium activities in the inside and in the outside solution has gone down from 5020 to 1.32, the ratio between the activities of calcium and potassium in the inside solution has decreased from 100 to 1.2.

Being in contact with a dilute salt solution containing both monovalent and bivalent cations, a slightly protolysed acidoid (dilute micellar solution) favours the entrance of the monovalent ions to a higher extent than does a strongly protolysed acidoid (concentrated micellar solution). Contrarious conditions prevail for the bivalent ions. Thus, the relative replacing power of monovalent and bivalent cations becomes dependent on the state of protolysation of the acidoid. This was demonstrated by MATTSON and LARSSON (1946) on electrodialysed bentonite which was treated with solutions containing equivalent quantities of NH_4Cl and $CaCl_2$ at varying acidity.

4. When dilution takes place, the concentration of the outside solution decreases much faster than that of the inside solution; practically, the increase of the volume of the micellar solution is greatly limited. As a result of dilution the ratio between the *f*-values of the bivalent ion in the outside and in the inside solution will increase faster than that of the monovalent ions. For this reason as well as on account of the fact that the root of the activity of the bivalent ion is used, a change in the ion distribution must take place in order to restore the equilibrium; this change implies an increase of the ratio $[\overset{++}{\mathrm{M}}]_i : [\overset{+}{\mathrm{M}}]_i$. A dilution of the outside solution obviously results in an increase of the relative concentration in the

inside solution of ions of high valence and a corresponding decrease of the concentration of the ions of low valence. When a Donnan system is concentrated this leads to a shifting in the opposite direction. Compare the computations above.

5. When x, y, and z are inserted into the Donnan equation for a uni-uni-valent salt, $x^2 = y(y+z)$, the following will be easily understood: The higher the value of z (increasing strength and concentration of the acidoid groups), the lower will be y in relation to x, i.e., the more irregular the distribution of the free electrolyte. When $z \rightarrow 0$, x and y tend to approach each other asymptotically, the ion distribution becomes homogeneous. The same situation arises when the outside concentration is very high. In this case, z becomes low in relation to x and y which approach each other.

Similar conclusions as have been presented regarding the ion distribution in acidoids may be drawn for basoids. However, there are considerably less experimental verifications of the validity of the Donnan equilibrium for basoids than for acidoids.

It looks as if the Donnan equilibrium could become an instrument of great value for the pedologist. Unfortunately, however, the soil colloids apparently deviate greatly from ideal systems and the quantitative application of the activity concept becomes then extremely difficult. Although the importance of activity has been emphasized among others by Teräsvuori (1930), Møller (1935), Mattson and Wiklander (1940) and most recently Davis (1945), no quantitative results in terms of activity have yet been presented. As long as it is impossible to determine with some degree of certainty, the activity coefficient of the different ions in the micellar solution, no reliable quantitative calculations will be possible. Important qualitative information may still be gained. Judging from the results of Samuelson (1944) the Donnan equilibrium may, nevertheless, in certain cases, be applied without paying consideration to the activity factors of the ions. This, however, is the case only when the micellar solution is dilute and the ions have the same valence.

In spite of the advantages offered by the Donnan equilibrium, its uncritical application may become misleading. There is no reason to expect a Donnan distribution of the ions, if the structure of the ion exchanger does not permit the free distribution of all the ions taking part in the equilibrium. At ion blockade, the diffusion of certain ions to and from the inner surfaces is partly checked; this must result in deviations from the Donnan equilibrium.

To work out empirical formulas exclusively aimed at covering experimental results in the best possible way without explaining the nature of the reaction, seems to me to be considerably less valuable than to explain the reactions and equilibrium conditions with the aid of theoretically founded formulas, even though this may only be done qualitatively. The intimate interrelation between

the relative ion composition of the micellar solution and the dilution in the presence of heterovalent ions is readily explained by the Donnan equation, as already shown. The hypothesis of »the salt-free water layer» which was laid down and defended by VAGELER (1932) (ALTEN and KURMIES 1935) and which is strongly contradictory to the Donnan equilibrium, provides no solution of this relationship. Furthermore, the hypothesis of the salt-free water layer must be considered to be disposed of for good by the work of DU RIETZ (1938) and SAMUELSON (1942 b, 1944), the latter having devoted much interest to the question.

The Donnan equilibrium has long been an object of attention from the side of certain pedologists, but only a few years ago its possibilities for elucidating the exchange reactions have begun to be utilized. Already in 1921, O. ARRHENIUS (1922) suggested that it might be possible to interpret the results of his investigations on the amphoteric reactions of clays with the aid of the Donnan equilibrium in the same way as LOEB (1921, 1922) had done for gelatine. It was mentioned by TIDMORE and PARKER (1924) that the Donnan equilibrium may be applied to acidoids in order to explain the decrease, from the surface outward, of the H-ion concentration in an acidoid particle. Later, the law has been used by TERÄSVUORI (1930) in connection with studies on the acidity in soils, by DU RIETZ (1938) in ion exchange investigations, by SAMUELSON (1944), WIKLANDER (1945) and above all by MATTSON and collaborators who, in a number of works (1929, 1940, 1942, 1946), has utilized Donnan's law of the unequal ion distribution in order to clear up several colloid reactions and thus to explain important soil processes.

III. The Relative pH-Reducing Power of the Alkali and Alkaline-Earth Ions in Electrodialysed Materials.

1. Introduction.

If various neutral salts with a common anion are added to a slightly protolysed H- and OH-saturated ampholytoid, an ion exchange takes place. The cations of the salt replace H and the anions of the salt replace OH. If the activity of the basoid part is lower than that of the acidoid part, the OH-replacement may be assumed to be approximatively equal for the various salts at corresponding concentrations. On the presumption that no side reactions occur,

which influence the acidity formed by the exchange, the decrease in pH becomes also an expression for the relative replacing power of the cations; the greater the exchange acidity, the greater the replacing power of the cations. This relation is true to a greater extent, the weaker the basoid properties and the more the ampholytoid approaches an »ideal» acidoid (»Ideal» defined in the following chapter). Even if the exchanger contains Al^{3+} and Fe^{3+} as a more or less substantial part of the exchangeable cations in addition to H, the approximative relationship between pH-decrease and relative replacing power holds true.

As shown by Kappen (1916), Paver and Marshall (1934), Alten and Kurmies (1935), Mukherjee and Chatterjee (1945) and others, base-unsaturated clays liberate Al when treated with neutral salts. The authors assert that the Al set free from the clay exists as exchangeable Al^{3+} and is not secondarily dissolved from the clay by the primarily replaced H-ions. Having studied these conditions in bentonite and Putnam clay Paver and Marshall maintain that unsaturated clays are to be regarded as H-Al-clays rather than as H-clays. According to Roemer and Scheffer (1944) and Mukherjee et al. Fe functions similar to Al. The hydrated Al and Fe ions replaced by the neutral salt react as free acids. On account of the fact that the $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ are rather weak acids, the exchange acidity becomes somewhat lower, and with this the pH higher, than if the exchangeable ions consisted of H only. The order of the relative replacing power of the cations as indicated by the pH is, however, not changed by this. Whether this relation between the pH-decrease and the relative replacing power holds true also in synthetic, inorganic exchangers is dependent on the extent to which possible side reactions, influencing the pH and specific for the various cations, take place.

Since it is of interest for the following treatment of the pH-decreasing power of neutral salts, some results of research in this sphere will be discussed briefly.

O. Arrhenius (1925) studied the effect of a number of neutral salts on the pH-value in soil suspensions. The soils investigated were a sandy soil, an acid and an alkaline clay, and a sphagnum peat soil. The added cations reduced the pH-value in the following order: $Na < K < NH_4 < Mg < Ca$.

Teräsvuori (1930) has devoted extensive studies to the acidity problem of the soil. He worked with both H-saturated soils (washed with 0.05 N. HCl) and soils that were more or less base saturated. Teräsvuori found that, irrespective of the type of cations originally held by the soil, the cations studied reduced the pH-value of the suspension in the following order: $Na < K < Mg < Ca$.

It is often maintained that bivalent ions generally have a more intense pH-reducing and ion-replacing effect than monovalent ones,

no attention however being paid to the question to what an extent the *nature* of the ion exchanging material or the *concentration* of the added salts might influence the result. Thus, MILLAR and TURK (1943), in their book »Fundamentals of Soil Science», assert that a listing of the more common cations in increasing order of replacing power is as follows: $Li < Na < NH_4 < K < Rb < Mg < Ca < Ba < Sr < H$.

In his well known textbook, ROBINSON (1937) maintains that the order of »absorption» of the principal cations by the colloidal complex is $Na < K < Mg < Ca < H$. The same order for the replacing power is also to be found in the book of LYON and BUCKMAN (1943). Moreover, ROBINSON, quoting JENNY (1927), gives the values for the exchange constants of the following ions against calcium permutite:

H	Li	Na	K	Rb	Cs
58.117	3.500	6.066	8.896	11.550	13.112

The correspondent constants for bivalent ions were:

Mg	Ca	Sr	Ba
29.801	48.128	49.882	69.137

Unfortunately, ROBINSON does not consider the fact that the exchange constants of the bivalent ions have been obtained by exchange with NH_4-permutite and those of the monovalent ions with Ca-permutite. The exchange constants of the monovalent and bivalent ions are therefore not comparable. ROBINSON's statement that »the figures give a measure of the energy of replacement of the different ions» leads to an erroneous view regarding the relative replacing power of these ions in permutite.

As a matter of fact, JENNY (1927) proved that, when the monovalent and bivalent ions were compared with each other by exchange against NH_4-permutite, the order changed with the concentration. At low concentrations all the bivalent ions were better adsorbed than monovalent ions. However, when the concentration increased the order was partly reversed.

JENNY found that when water and different 0.02 N. chlorides were added to H-saturated permutite, the pH-values were reduced in the following order:

H_2O	$Li < Na < Mg < Ca < K = Ba < NH_4 < Rb < Cs$								
pH 4.70	4.48	4.46	4.36	4.30	4.25	4.25	4.22	4.20	4.10

With regard to the relative pH-reducing effect and the replacing power of the alkali and alkaline-earth ions it may be stated that so far no general systematic investigation has been made on these.

Considering the different nature of the ion exchangers, e.g. organic or inorganic, amorphous or crystalline structure, different lattice type, inner and outer surfaces etc., as well as the complicated activity conditions for colloid ions and electrolytes, it may be expected a priori that the relative pH-decreasing effect and replacing power of the ions will by no means always be the same, as already indicated by the results with permutite. In the present investigation I have tried to throw light on these questions by examining several electrodialysed or »isoelectrically» precipitated substances of different character and origin with regard to the pH-reducing power of the cations mentioned below. Throughout, chlorides of Li, Na, K, Mg, Ca, Sr, and Ba have been used as neutral salts, as a rule in the concentrations 0.001, 0.01, 0.1, and 1 N. For comparison with the monovalent and bivalent ions, the trivalent La has been included. Surely, the La-salts are somewhat hydrolysed, but not to such an extent that $LaCl_3$ could not be considered as a neutral salt at the range of pH covered in the experiments.

2. Theoretical Points of View.

An »ideal» acidoid is supposed in the following considerations. An acidoid is here considered to be »ideal» if its ion exchanging groups are uniformly distributed on the surface, possess the same dissociation constant, and are easily accessible to all cations added. Moreover, the supposition is made that no lattice ion exchange and no specific reactions can take place.

When a neutral salt is added to such an acidoid, ionic exchange occurs causing the H-ions to migrate into the outside solution. The extent of the pH-reduction caused hereby depends on the strength and the concentration of the acidoid as well as on the concentration and replacing power of the cation added. For a given acidoid and a certain salt concentration the activity coefficient (f) of the cation of the salt and that of the H-ion will consequently determine the size of the exchange acidity. If one imagines an infinitely dilute outside solution, the activity coefficient of all the ions to be found there will be 1. When a cation passes from the outside into the inside solution it meets a more and more increasing ionic strength which reaches its maximum on the surface of the colloid ion. The decrease of the activity coefficient of the cation resulting from this passage is different for the various ions and progresses, for reasons discussed in part II : 9, in the following order for the ions concerned here:

$$Li < Na < K < Mg < Ca < Sr < Ba < La.$$

The added salt replaces some of the H-ions and increases the ionic strength of the micellar solution, whereby the activity of the acidoid

ion and the H-ions in the micellar solution is temporarily reduced. In order to restore the equilibrium a further protolysation of the acidoid takes place. The latter appears to become stronger. Since the activity coefficient may be considered a measure of the interionic forces — these are the greater, the lower the activity coefficient — an ion with a lower *f*-value will cause a more intense protolysation of the acidoid than an ion with a higher *f*-value and thus bring about a stronger H-replacement.

It appears from what was said above that *the H-ion exchange*, *the increased protolysation* of the acidoid, and *the pH-reduction* in the outside solution *increase* in *the above-named order* which coincides with the lyotropic series.

Similar conclusions may be reached by directly applying the Donnan equilibrium to the exchange reactions in the way described before; by this the influence of the valency of the cation on the H-replacement becomes clear.

It is due to several reasons that one has to expect greater or smaller deviations of the ionic exchange in real acidoids from that in the »ideal» acidoid outlined here. Deviations may be explained by:

1. the structure. The influence of the structure may become manifest in such a way that the diffusion of the ions to and from the ion exchanging surfaces is more or less obstructed or made entirely impossible with regard to a certain part of the surface, ion blockade;
2. more or less extensive fixation of the added cations in the crystal lattice of the exchanger;
3. an »abnormal» variation of the activity coefficients of the exchanging ions; this phenomenon largely depends on the concentration of the salt;
4. side reactions. The conditions in some ion exchangers often indicate the influence of reactions of unknown nature which may be characterized as something specific in the behaviour of an ion towards a certain ion exchanger.

A priori, it may be expected that among the exchangers examined here the humus material will be the one to come nearest to the ideal acidoid in regard to the ion exchange properties. All ion exchanging groups are likely to be easily accessible to added cations and there will be scarcely any lattice reactions. Even kaolinite with its outer-surface ion exchange and montmorillonite with its open lattice-structure may be expected not do differ to any greater extent from the ideal acidoid regarding the conditions concerned here. Permutites, on the other hand, ought to show considerable divergences on account of their heterodispersed and undefined structure.

3. Materials Investigated.

Here follows a short description of the exchangers studied in this part. In order to give a general character to the investigation on the relative pH-reducing effect of the cations several exchangers of various nature and origin, both inorganic and organic as well as synthetic and natural ones, have been included.

The ion exchanging material which was not »isoelectrically» precipitated was freed from cations and anions by electrodialysis in a MATTSON cell (1926). The voltage was regulated in such a way that no considerable heating of the cells took place. Thus the changes in the composition and structure of the ion exchanging materials may be supposed to be the least possible. The progress of the electrodialysis was supervised partly by control of the current and partly by titration of the cathode-water with phenolphthalein (PP) as indicator. The layer nearest to the cathode-membrane was thrown away, the rest was dried at 30—35° C, cautiously pulverized in the agate-mortar and thoroughly mixed. All silicates and phosphates were subjected to chemical analysis. For this the silicates were dissolved in HCl, whereafter Al, Fe and Si were determined as oxides (HILLEBRAND and LUNDELL 1929). In the phosphates P was determined colourimetrically (SCHEEL 1936); Fe was reduced with cadmium according to TREADWELL (EGNÉR 1929) and titrated with $KMnO_4$; Al was precipitated as $AlPO_4$ according to HILLEBRAND and LUNDELL. The composition is calculated on the air-dried sample.

1. Humus F_2 from the raw humus layer of the Häggbygget podzol profile, to a depth of 2—5 cm, described by MATTSON and GUSTAFSSON (1935). Sticks and roots being sifted away the humus was electrodialysed. Pulverization was not necessary on account of the high degree of humification. In the electrodialysis the highly dispersed humus acids were removed; for this reason, the material used in the investigation mainly consisted of real acidoids. The loss on ignition amounted to 94 %, so that the acidoids practically were of a completely organic character.

2. Litter of leaves ($= F_0$) from newly fallen birch leaves, ground and electrodialysed.

3. Aluminium phosphate. The phosphate was produced by »isoelectric» precipitation in the following way: 500 mmol $AlCl_3$, dissolved in 20 l of distilled water, were poured down under stirring into a solution of 500 mmol $(NH_4)_2HPO_4$ + 580 mmol NH_4OH in 20 l of distilled water. The pH-value in the clear solution was 5.07. After being decanted and washed until all chloride was removed the phosphate was filtered, dried at 30—35° C and pulverized. Composition: $Al_2O_3 \cdot (P_2O_5)_{0.96} \cdot (H_2O)_{4.42}$.

4. Ferriphosphate. The phosphate was of the quality DAP.V; it was electrodialysed, dried and pulverized in the way mentioned. Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.97} \cdot (H_2O)_{4.15}$.

5. Aluminium silicate I. The anionic component for the preparation was metasilicate, which by analysis was found to have the composition $Na_2SiO_3 \cdot 9\,H_2O$. 284 g of sodium silicate were dissolved in 5 l of distilled water and quickly mixed under stirring with an equivalent amount of $AlCl_3$ dissolved in 15 l of distilled water. By adding an appropriate amount of NaOH to the Na-silicate solution the precipitate was formed at pH 4.40. After repeated decantation, until practically all chloride was removed, and subsequent filtration the colloid was dried and ground in the agate mortar. In spite of thorough washing the Al-silicate was found to obtain small amounts of Na. Part of the Na was set free on drying — the colloid hereby looses part of its activity — and was therefore removed by a short electrodialysis. Composition: $Al_2O_3 \cdot (SiO_2)_{2.73} \cdot (H_2O)_{9.1}$.

6. Aluminium silicate II. The commercial silicate was electrodialysed, dried and pulverized. Composition: $Al_2O_3 \cdot (SiO_2)_{3.97} \cdot (H_2O)_{4.59}$.

7. Aluminium silicate III. The silicate was precipitated at pH 4.41 in the same way as the aluminium silicate I. The precipitate was washed by decantation until all chloride was removed. In order to study the effect of drying of a silicate gel on its ion exchange properties, the silicate was not filtered and dried before using. Composition: $Al_2O_3 \cdot (SiO_2)_{2.22} \cdot n\,H_2O$. The aluminium silicates I and III possess rather similar composition. As far as there is any greater difference with regard to certain properties, it must be ascribed to the fact that the latter has always been kept under water while the former has been subjected to the drying procedure.

8. Ferrisilicate. The commercial silicate was electrodialysed, dried and ground. Composition: $Fe_2O_3 \cdot (SiO_2)_{7.31} \cdot (H_2O)_{4.17}$.

9. Na-permutite. The permutite was rather coarse and was therefore ground; it was sifted through a 0.2 mm sieve and subsequently electrodialysed and pulverized anew. It appeared necessary to stir up the permutite repeatedly during the electrodialysis as was described before. Composition: $Al_2O_3 \cdot (SiO_2)_{6.87} \cdot (H_2O)_{6.61}$.

10. Bentonite from the firm of J. D. Riedel — E. de Haën A.-G., Berlin. The bentonite which was very finely ground was electrodialysed and pulverized. Bentonite which is a natural product consists mainly of the mineral montmorillonite.

11. Kaolinite. The kaolinite, which had been washed in acid and finely ground, was electrodialysed and pulverized.

12. Two bleaching earths for bleaching of oil.

a. German bleaching earth 1, activated with sulphuric acid.

b. German bleaching earth 2, activated with hydrochloric acid.

Both samples were electrodialysed. Their mechanical composition is shown in table 3.

13. Four mineral-soils.
a. Surface soil from Sperlingsholm, Hallands län.
b. Surface soil from Fristorp, Älvsborgs län.
c. Surface soil from Kungsängen, Uppsala län.
d. Subsoil, Ancylus clay from Ärna, Uppsala län.

All soils were electrodialysed. The mechanical composition and the contents of organic matter are shown in table 3.

Table 3. *Mechanical composition of the soils used in % of dry matter.*

Soil	Coarse sand 2–0.2 mm	Fine sand 0.2–0.02 mm	Silt 0.02–0.002 mm	Clay < 0.002 mm	Org. matter	Total
German bleaching earth 1	0.5	14.9	44.4	41.5	0.0	101.3
German bleaching earth 2	0.8	35.6	58.7	5.6	0.0	100.7
Soil from Sperlingsholm	1.3	54.1	17.7	21.5	4.8	99.4
» » Fristorp	8.4	32.5	27.7	26.2	4.3	99.1
» » Kungsängen	2.3	8.4	40.2	44.5	5.2	100.6
Ancylus clay from Ärna	0.6	2.2	10.4	85.6	0.0	98.8

The mechanical analysis was carried out according to the pipette method of Robinson (Robinson and Richardson 1933) and the contents of organic matter were, according to Ekström (1927), considered equal to the reduced loss on ignition.

4. Experimental Methods.

All pH-determinations have been done potentiometrically either by quinhydrone or by glass electrode. For measurements with the aid of the former, a quinhydrone electrode with Veibel standard (0.01 N. HCl + 0.09 N. KCl, pH = 2.04) as solution was used as comparing electrode (Biilmann 1927). The pH-values were calculated according to the formula for concentration-elements (Clark 1928) which in the present case and at a temperature of 20° C may be simplified as to read:

$$\mathrm{pH} = 2.04 + \frac{\mathrm{mV}}{58.1},$$

where mV denotes millivolts.

It is well known that the applicability of the quinhydrone electrode is limited. At not too high pH-values (approximatively < 8) oxidizing and reducing substances form the greatest sources of errors.

In those cases when the quinhydrone electrode proved to be useless or when it had not been fully reliable, Beckmann's glass electrode potentiometer with saturated calomel electrode as comparing electrode was used.

Besides the above-named incorrectnesses, the quinhydrone electrode is even subjected to »salt errors» which, according to Hovorka and Dearing (1935) increase almost proportionally with the concentration of the disturbing substance. »Salt errors» are due to the fact that the activity coefficients of the quinone- and hydroquinone-components do not vary in the same degree when the salt concentration changes (Biilmann 1927). As shown by Hovorka and Dearing (1935) for a great number of chlorides and sulphates, the different cations have but low specific effect and only the anions have therefore to be considered. However, no correction of the values obtained has been introduced, since the »salt error»[1] is minute, the anion was everywhere the same, and the pH-determinations in this section are intended in the first place to yield such values as may be reciprocally compared at every concentration.

The diffusion potential was kept as low as possible by using an agar-bridge with saturated potassium chloride. During the measurements the bridge was repeatedly exchanged and at every such exchange, as well as in between, the apparatus was controlled with buffer solutions of known pH-value.

The suspension effect has been kept constant by agitating with a rotating glass propeller. The term suspension effect is used to describe those cases when the pH in the suspension and in the suspension medium becomes more or less different on account of the inhomogeneous ion distribution at the boundary between the solid (suspended) particles and the surrounding solution, Wiegner and Pallmann (1929), Du Rietz (1934).

In those series where the quinhydrone electrode could not be used and the sedimentation effect made a direct determination with the glass electrode uncertain, the suspensions were centrifuged, after which the pH-value was measured in the ordinary way in the clear solution with the aid of Beckmann's glass electrode potentiometer. The application of the glass electrode as used in the Beckmann apparatus implies sensibility for the suspension effect because agitation is impossible. Also Bailey (1943) has made similar observations with the glass electrode. If the suspension is poor in salt and the inside concentration (z) is high, as well as when the suspensoid sedimentates quickly, it often happens that no constant values are obtained but that the potential shows a more or less rapid change. At higher salt contents, however, the result becomes better because

[1] According to Hovorka and Dearing (1935) the error amounts in a 1 N. solution (this is the highest concentration used here) to -0.040 pH-units for Cl^- and to $+0.024$ pH-units for SO_4^{2-}.

the salt reduces the Donnan potential. When determination takes place in the clear centrifugate, no disturbances occur and well reproducable pH-values are obtained. When the measurements were taken, the electrodes were washed with the solution; several parallels were taken and the apparatus was controlled with buffer solutions the pH-values of which lay within the measuring range.

The glass electrode, too, is subjected to »salt errors» but these, according to Dole (1931, 1941) and Du Rietz (1937), generally seem to be confined to the alkali cations and to pH-values above 9. The Na-ion, in particular, may cause considerable errors at high concentration and high pH-values. However, the pH-determinations made in this investigations all fall within the error-free range of the electrode.

In all pH-series for a certain material the ratio between substance and solution was constant, as a rule 1:10. For the soils a 1:2 ratio was used since these soils have a considerably lower exchange capacity than most of the other ion exchanging materials. After solids and solution had been mixed, shaking took place in a rotating shaking machine according to Wagner for three hours on the first day and another two hours on the following day. The total time of reaction between substrate and solution amounted to about 24 hours. All the time the temperature was kept at $20 \pm 0.5°$ C, the work being done in a room with constant temperature. All the series which were to be compared were prepared and shaken at the same time. Even the pH-determinations were made at the same time and in the same way. In order to obtain the most reliable results, the pH-values for a certain salt concentration were always determined in the sequence: Li, Na, K, Mg, Ca, Sr, Ba, and La. The beginning was made with the »water-value», and then followed the concentrations 0.001, 0.01, 0.1 and 1.0 N. By this procedure it was possible to keep down the experimental errors and to arrive at a considerably higher degree of exactness than otherwise would be the case, particularly because the relative pH-reducing effect of the cations was of greater interest than the absolute effect. By repeated measurements it could be established that the error as to the difference between the pH-values of two cations ranged within the limits $pH_{M_1} - pH_{M_2} = \pm 0.02$.

5. Time Necessary for the Accomplishment of the Equilibrium.

It has been shown by Wiegner and collaborators (Cernescu 1933, Wiegner 1936) and most recently by Damsgaard-Sørensen (1941) that ionic exchange is a reaction requiring much time in some ion exchangers. Cernescu has shown that the reaction velocity is strongly influenced by the structure of the colloid particles. In materials which do not swell up in water and which possess plenty

of inner surfaces, the diffusion ways of the ions become long, so that more time is required for accomplishing the equilibrium than for particles with exclusively outer surfaces and short diffusion ways. To the former type belongs chabasite, to the latter kaolinite. Permutite takes an intermediate position.

If ion exchange is in fact a reaction requiring time, the pH-value measured may be expected to be a function of the time of reaction between the substance and the salt solution. For an acidoid the pH will fall quickly in the beginning and subsequently approach more and more slowly a certain final value. If the substance has a sponge-like structure, ions with a low diffusion velocity may be expected a priori to give rise to flatter curves than ions with high velocity, provided that no ion blockade occurs. The time required should be longer for ion exchanging material possessing inner surfaces than for substances with only outer surfaces.

The conditions have been studied by the following experiments with *H-saturated permutite* and *humus* F_2. Two cations with extremely low (potassium) and extremely high (magnesium) volume of the hydrated ion were chosen; compare the hydration figures in table 2, part II. Thus any possible effect of the volume of the ions on the reaction velocity may be expected to become evident most easily. In contrast to permutite with its spongelike structure, the humus was considered to be chiefly built in such a way that the ionogen groups were directly accessible to the salt added. Therefore, no diffusion process requiring more or less time ought to precede the ion exchange which consequently might be expected to occur very rapidly.

1.00 g portions were weighed into ordinary pH-tubes whereafter 5 ml of distilled water were added to each tube. The period of reaction between water and ion exchanger thus became equal for all samples. 5 ml of 0.2 N. salt solution were added to the different tubes at 24, 2, 1/2, and 1/60 hours previous to the pH measurements which all were made at the same time. The time of shaking was 24 hours and the only difference between the samples were therefore the variations of the time of reaction between the salt and the ion exchanger. The results obtained are shown in table 4.

It appears that the differences of the pH-values at different times are minute. Permutite yields identical values everywhere with KCl. With $MgCl_2$ the pH has become somewhat lower after 24 hours. In contrast to the expectations, the pH of humus seems to depend to a certain extent on the time of reaction with both KCl and $MgCl_2$. In conformity with the considerations made earlier there is some indication that the duration of the time of reaction is of inferior importance for the K-ion than for the Mg-ion. Yet the differences are so small as to fall within the limits of the experimental error. From the experiment the conclusion may be drawn that, under the

Table 4. *Effect of variations in the time of reaction between neutral salts and H-saturated ion exchangers on the pH-value measured in the suspension. pH in water for permutite was 4.74 and for humus 2.96. Quinhydrone electrode.*

Hours between addition of salt and pH-determination	Permutite in		Humus F_2 in	
	KCl 0.1 N.	$MgCl_2$ 0.1 N.	KCl 0.1 N.	$MgCl_2$ 0.1 N.
1/60	3.77	4.01	2.41	2.41
1/2	3.77	4.01	—	—
2	3.77	4.01	2.41	2.37
24	3.77	3.99	2.37	2.36

conditions of the test, it does not matter, if pH is determined immediately after the salt is added or one day later, irrespective if a substance of a sponge-like structure, permutite, is concerned or an organic material. Naturally, the material must be well moistened at the time when the salt is added. However, for all the pH determinations made in this part of the work the time of reaction has been extended to 24 hours.

Also Gedroiz (1931) and Nachod and Wood (1944), while studying the reaction velocity of ion exchange, have found that the equilibrium is quickly reached.

6. Experimental Results.

A. *pH in neutral salt solutions.*

The results of the pH-determinations are, as a rule, presented only graphically. In order not to overburden the context unnecessarily, all tables which are not indispensable for understanding the experimental results and the context as a whole have been omitted.

Humus F_2.

pH-series with LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, and $LaCl_3$ were prepared as described above. 1.50 g substance in 10 ml solution. The quinhydrone electrode was used for the pH determination. The results are shown in figure 5. It must be mentioned here that on the abscissa the negative logarithms of the added salt are recorded and not the equilibrium concentration. On account of the ion exchange taking place, the difference may, at high dilution, become considerable as far as the absolute and relative position of the curves is concerned but, still, the order will not be changed. The somewhat s-shaped course may, to a certain extent, be caused by the fact that the points for 0.001 N. are, for the aforementioned reason, situated too far to the right. ∞ denotes no addition of salt.

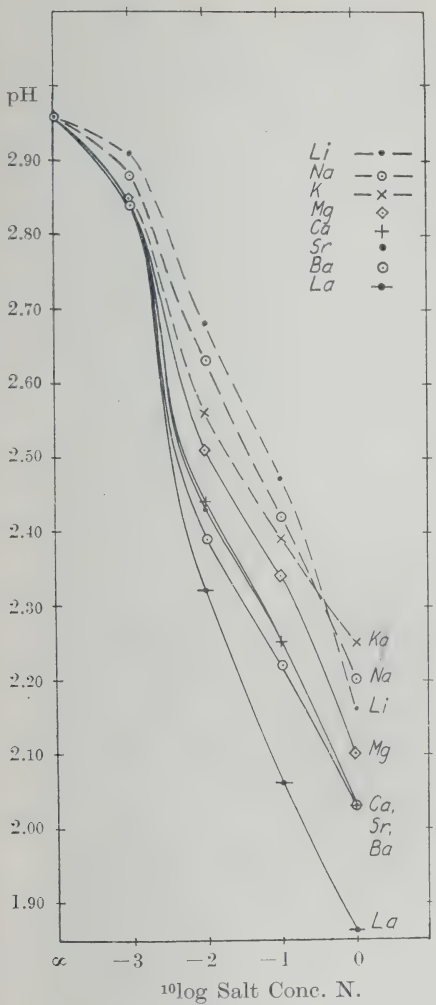


Fig. 5. pH of electrodialysed humus F_2 in chloride solutions of Li, Na, K, Mg, Ca, Sr, Ba, and La at varying concentrations. 1.5 g substance in 10.0 ml solution.

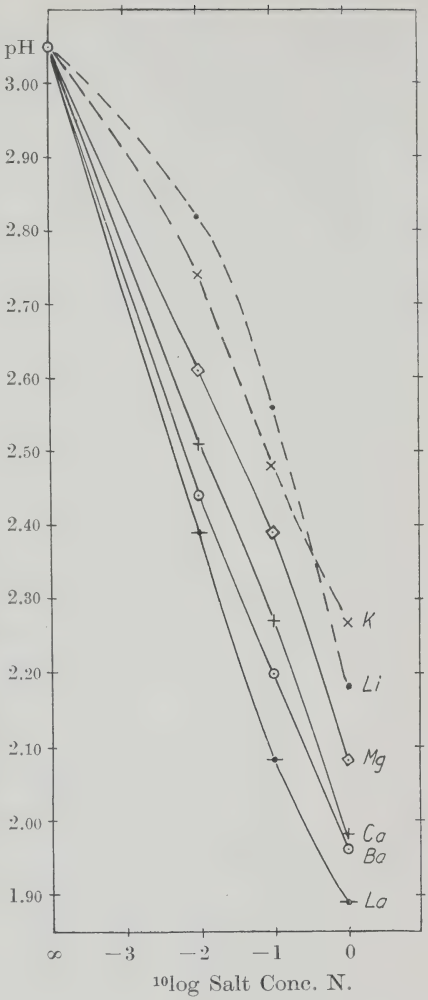


Fig. 6. Litter of birch leaves. pH in the same concentration series as in fig. 5, Na and Sr excepted. 1.0 g substance in 10.0 ml solution.

The following appears from figure 5:

1. In all concentrations pH is reduced less by monovalent than by bivalent cations and less by bivalent than by trivalent ones. At concentrations up to 0.1 N. the order is in complete agreement with

the lyotropic series and with the conditions prevailing in an ideal acidoid: $Li < Na < K < Mg < Ca < Sr < Ba < La$. Consequently, humus behaves here as an ideal acidoid in which an ion may be expected to be bound the better, the lower its activity coefficient in the inside solution.

2. The curves of the alkali ions show a strange course. At the three lowest concentrations the order, as expected, is: $Li < Na < K$, at the highest concentration, on the other hand, it is reversed: $Li > Na > K$. Therefore, if the pH of the humus had been determined first in 0.01 N. NaCl and KCl and thereafter in 1.0 N. solutions, the pH would have been higher in the first case in NaCl than in KCl but lower in the second case. At first sight, this result seems to be paradoxical but, at closer examination, it is nevertheless possible to explain the phenomenon. The whole effect may be interpreted as being caused by hydration of the cations and an ensuing rapid change of the activity coefficients.

As mentioned before, the activity coefficient may at high concentrations pass through a minimum and, subsequently, rise to values which sometimes may lie considerably above 1. This is considered to be due to the fact that, by becoming hydrated, the ions occupy the solvent, so that the concentration appears to be higher than calculated (Getman and Daniels 1937). In high concentrations the variations may be considerable. The effect is more marked for strongly than for slightly hydrated ions and becomes manifest in the experimentally determined $f_{\pm}$-values. The more hydrophile a salt is, the lower is the concentration at which its $f_{min.}$ value appears. The same seems to apply to ions. These conditions are illustrated by figures 2 and 3. Compare also Lewis and Randall (1923).

It appears from figure 2 that $f_{\pm\ min.}$ lies at about 0.5 N. for LiCl, 1.2 N. for NaCl, and 2.4 N. for KCl. It will be seen in figure 3 that the activity coefficient of Li forms a minimum-curve and that those of Na and K have the same tendency. The very great difference between the f-values of the cations appearing already in the 1 N. solution is remarkable. Analogous conditions prevail for Mg, Ca, Sr and Ba but $f_{min.}$ lies at considerably lower values than for the alkali ions.

By an interpretation of the curves in figure 3 it is possible to give a plausible explanation of the reversal of the Li-, Na- and K-curves in the experiment. The humus acidoid is a rather strong acidoid — compare point 4 below — for which reason it is likely to possess a micellar solution with high ionic strength already in pure water. Thus, when the salt concentration increases, the ionic strength of the outside solution grows much faster than that of the inside solution. The changes of the f-values in the inside solution are consequently inconsiderable compared with those in the outside solution.

On account of the fact that in the outside solution at concentrations above 0.15—0.2 N. the difference $f_{Li} - f_{Na}$ grows quickly and much faster than the difference $f_{Na} - f_K$, the activity in the outside solution and, with this, the relative increase of the replacing power grow rapidly in the order: $K < Na < Li$. A very important additional factor is the rapid increase in the order $K < Na < Li$ of f_H in the outside solution at concentrations above 0.15 N.; this leads to an increase of the activity of the replaced H-ions in the same sequence. The conditions of the alkali cations and the H-ions apparently work together in causing the intensity of the exchange acidity to change from the order $Li < Na < K$ to $K < Na < Li$ within the range of 0.1 to 1.0 N. solution. This anomaly may have been accentuated a little by the fact that the water adsorbed by the humus contains less of the free electrolytes (i.e. $y < x$), thus increasing the concentration of the outside solution.

The same tendency may, after all, be traced in the bivalent group though the phenomenon, there, is considerably less pronounced.

3. The Ca- and Sr-curves lie very closely together. Compare the results from Al-phosphate, page 59.

4. From the steep course of the pH-curves in fig. 5 — here it should be observed that the curves on the whole cover a low part on the pH-scale — it may be concluded that the humus acidoid is rather strong. The low pH-value in water is presumably caused by a high suspension effect, indicating a high inside concentration (z_H), and by the fact that some acids have been solved out.

Litter of birch-leaves.

On account of the limited amount of material available the experiments with NaCl and $SrCl_2$ were excluded here as well as the 0.001 N. solutions. The suspensions were all made 1:10 and the quinhydrone electrode was used. The results appeared to be in complete agreement with those obtained with humus F_2. Figure 6.

It is interesting to note that the litter behaves like humus from a podzol profile in spite of the great differences in the parent material and the degree of transformation.

Schachtschabel (1940) found a considerable »selective» adsorption in the humus substances »Huminsäure Merck» and »Kasseler Braun» as well as in organic soil colloids. After leaching with neutral Ca-NH_4-acetate solution ($Ca = NH_4 = 0.05$ N.) about 92 % Ca but only 8 % NH_4 were adsorbed. From his other results Schachtschabel gained the conviction that from the point of view of colloid chemistry the NH_4- and K-ions could be considered equal, so that even Ca and K would have caused a similar selective sorption. Schachtschabel explained the strong adsorption of Ca as being a purely chemical phenomenon depending on the low solubility of the Ca-humate as compared with that of the NH_4-humate.

My experiments, on the contrary, showed no »selective» adsorption by the organic materials investigated. It may be imagined that combinations difficult to dissolve may arise at pH-values about the neutral point but not at pH-values prevailing in the micellar solution in the unneutralized humus material. However, it seems most reasonable to explain the »selective» adsorption as a manifestation of the dilution effect in the Donnan equilibrium. If SCHACHTSCHABEL had leached with a more concentrated solution, then the ratio between adsorbed Ca and NH_4 would probably have decreased. Compare part II : 10 and VII.

Aluminium phosphate.

Similar pH-series as for humus have been executed with the synthetic phosphate. The results are presented in figure 7.

The following results may be gathered from the figure:

1. Within the alkaline ion group the replacing power lies in the order $Li < Na < K$ over the whole concentration range.

2. The alkaline-earth ions mutually behave in the same way: $Mg < Ca < Sr < Ba$. The difference between Mg and Ca is rather great, 0.30 pH-units in 1 N. solution. On the other hand, Ca and Sr are lying very closely together as is also the case in other materials. The distance between Sr and Ba is great, 0.42 pH-units.

3. Moreover, we find the following deviations from the lyotropic series: $Mg < Li$; $Mg < Ca < Na$; $Mg < Ca < Sr < K$.

It is surprising that Li is ahead of Mg and Na of Ca because both Li and Na are considered to possess low adsorption tendency.

4. That La enters more strongly than Ba is in accordance with the valence-rule saying that an ion is bound the more strongly the higher its valence.

5. The Mg- and Li-series show a strange course. After having reached a maximum of the exchange alkalinity in 0.1 N. the alkalinity decreases and, with regard to Li, passes into exchange acidity. It is not easy to explain why these salts, especially $MgCl_2$, react in an exchange-alkaline way. It appears from figure 8 that the same conditions are prevailing in the Fe-*phosphate;* however, this is not the case in the Al- and Fe-*silicates*. (Fig. 9 and 12.) From this the conclusion may be drawn that the anomaly must be due to a combined effect of LiCl and $MgCl_2$ and the phosphate groups. It is rather unlikely that the irregular course should be caused by inaccuracies of the electrodes, since the same results have been obtained by repeating the experiments, and the quinhydrone electrode was used for the Al-phosphate but the glass electrode for the Fe-phosphate.

As to their chemical properties, Li and Mg show great likeness in many respects. Both form difficultly soluble triphosphates. In

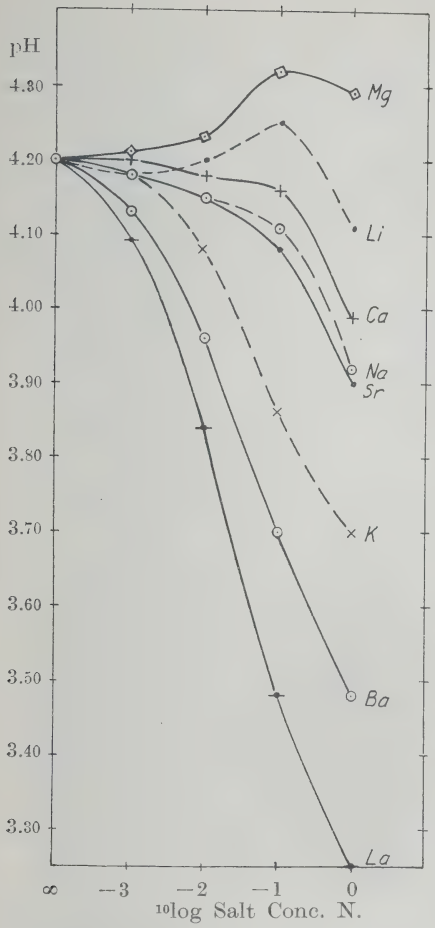


Fig. 7. pH of aluminium phosphate in the same solutions as in fig. 5. 1.0 g substance in 10.0 ml solution.

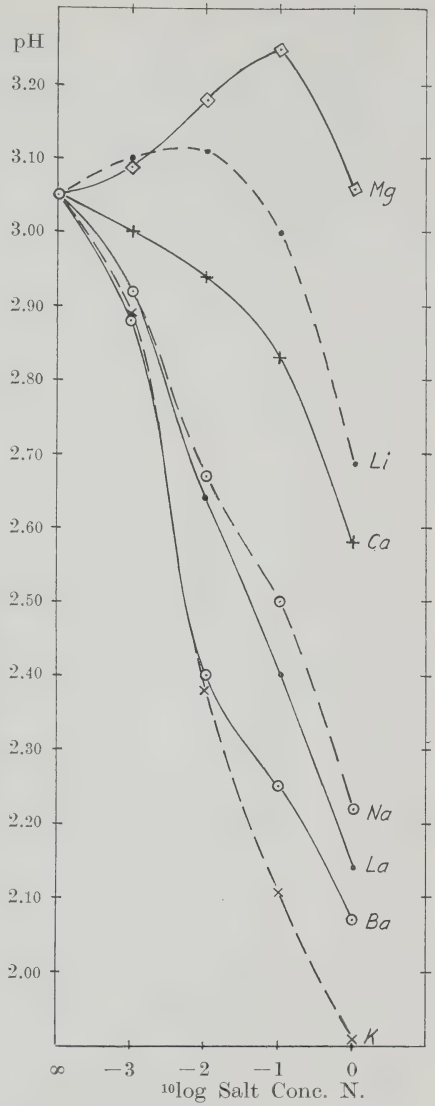


Fig. 8. Ferriphosphate. pH series the same as in fig. 7. Sr excluded.

any case, however, it is hard to imagine any reaction between either of the cations and the phosphate complex which would not lead to exchange acidity.

6. When the monovalent as well as the bivalent ions are arranged according to their pH-reducing effect, the following sequence is obtained: $Mg < Li < Ca < Na \leqq Sr < K < Ba < La$.

Ferriphosphate.

Series similar to those of Al-phosphate have been studied. Here, the quinhydrone electrode could not be used and was replaced by the glass electrode. The pH was determined in the suspension. The results appear in figure 8.

The following conclusions may be drawn from the figure:

1. The same anomalies regarding Li and Mg are to be found here as described above with the only difference that they are considerably more marked.

2. K and Na decrease the pH much more strongly, both absolutely and in relation to the polyvalent ions, than was the case in Al-phosphate. There, the following order was valid over the whole concentration range: $K < Ba < La$; here the order is: $La < Ba < K$. With Al-phosphate the difference in a 1.0 N. solution between $pH_{Na} - pH_{La}$ was 0.67 while with ferriphosphate the difference was only 0.08.

3. With regard to the pH-reducing effect at concentrations above 0.001 N. the cations investigated may be arranged in the following order: $Mg < Li < Ca < Na < La < Ba < K$.

4. When the figures 7 and 8 are compared we find a considerably lower pH in water for Fe-phosphate than for Al-phosphate. It also shows a greater exchange acidity. This is in agreement with the fact that $Fe(OH)_3$ is a considerably weaker base than $Al(OH)_3$ and therefore at corresponding pH neutralizes a minor part of the phosphoric acid. Moreover the ratio $P_2O_5 : Fe_2O_3$ is a little higher than the ratio $P_2O_5 : Al_2O_3$. Thus the active acidoid becomes greater in the former case than in the latter.

There is reason to wonder how the mentioned great deviations from the exchange conditions in an »ideal» acidoid and the humus may arise. At the low pH-values prevailing in several of the series the hydrochloric acid formed by the exchange reaction may have dissolved some of the iron in the phosphate. But, since $Fe(H_2O)_6^{3+}$ formed hereby functions as an acid, part of the hydrochloric acid is formed anew. Apart from the dissolving reaction, even an adsorption of Cl-ions by way of exchange against OH-ions may have taken place. However, it is difficult to understand how these processes have been able to influence the exchange to lead to such deviations.

A more plausible explanation might be that, schematically, the phosphate complex is partly dissolved by hydrolysis at which phosphoric acid and $Fe(OH)_3$ are produced; the $Fe(OH)_3$ then reacts with HCl, formed by the direct cation exchange. If the degree of this hydrolysis is influenced to a varying extent by the salts, it might be assumed that those salts which cause the greatest pH-reduction also cause the greatest hydrolysis. Consequently, this should have

been more extensive in KCl than in the other salts and stronger in NaCl than in $CaCl_2$. These conditions were examined for the Al- as well as the Fe-phosphate in 0.1 and 1 N. NaCl and $CaCl_2$ resp. The phosphate concentration and the shaking were the same as for the pH series. After filtering, the dissolved phosphoric acid was determined according to SCHEEL (1936); Fe was estimated colourimetrically with thiocyanate (SNELL and SNELL 1939). Al was not determined. Dissolved P, reported as P_2O_5 in pro mille of air dried matter, and Fe, reported as coloration of solution, appear in the following tabulation.

Added salt	Al-phosphate	Fe-phosphate	
	P_2O_5	Fe	P_2O_5
NaCl 0.1 N.	0.17	nil	0.29
» 1 »	0.26	slight trace	0.31
$CaCl_2$ 0.1 N.	0.23	nil	0.48
» 1 »	0.34	trace	0.59

If the table is compared with the pH-curves for NaCl and $CaCl_2$ in figures 7 and 8, it is evident that there exists no positive correlation between the dissolving power and the pH-reducing effect of the two salts. In spite of the fact that NaCl reduced the pH more than $CaCl_2$, there was less P and Fe liberated in the presence of the former salt than in the presence of the latter. It is to be noted that only traces of Fe were set free indicating a very small exchange of Fe^{3+} or liberation of Fe by hydrolysis or by dissolution.

A possible influence of blockade effect on the exchange reactions will be discussed below.

Al-silicate I.

pH-series have been made as with the preceding materials. pH was determined in the clear centrifugate with the aid of the glass electrode. The results appear in figure 9.

1. The Al-silicate I apparently behaves in many respects differently from the phosphate. No salt causes exchange alkalinity, the pH decreasing rapidly from the start.

2. The order of the alkali ions is in agreement with the lyotropic series. The difference between them is extraordinarily great as far as the pH-reducing effect at different concentrations is concerned. While at 0.01 N. the distance between Li and K is 0.64 pH-units and between Na and K 0.42, the distance at 1.0 N. is reduced to 0.22 and 0.09 respectively. The rapidly increasing *f*-values of the Na

and particularly the Li probably produce a certain effect on the exchange acidity at the high concentrations. Still this effect is not so pronounced in a silicate of the type used here — most of the pH-values are relatively high — since the inside solution of the silicate in water is likely to be considerably more dilute than was the case in the humus materials investigated. Therefore, the difference between the increase in concentration of the outside and that of the inside solution does not become so great when the salt concentration grows. The fact that the Li-curve intersects the Mg-curve may be explained at least partly by the more rapid growth of f_{Li} in 1.0 N. solution as compared with f_{Mg}.

3. Within the alkaline-earth group the curves show the expected course. As in the ion exchanging substances investigated above the difference between Ca and Sr is insignificant.

4. At 0.001 N. the order is as follows: $Li < Na < Mg < Ca < Sr = K < Ba < La$.

But at 1.0 N. it is: $Mg < Li < Ca \leqq Sr < La < Ba \leqq Na < K$.

In the first case, the agreement with the lyotropic series is rather good, the only exception being K which lies lower than Mg, Ca, and Sr. But already at 0.01 N. K has entered more strongly than both Ba and La and at 0.1 N. K has strongly increased its advantage. Later also, we will often find that, at not too low concentrations, K decreases the pH considerably more strongly than both Ba and La. By comparing the position of Na, K, Mg, Ba, and La in figures 5, 6, 7, 8, and 9, at first in 0.01 N. and then in 1.0 N. solution, the important rôle played by the ion exchanging substance for the relative pH-reducing power is revealed as well as the effect exerted by the concentration. It is therefore impossible to propose a general order for the pH-reducing effect of the cations, since such an order would in many cases prove to be completely misleading.

There is no quite satisfactory explanation of these strange ion exchanging conditions. It is probable that in humus ion exchange takes place without interference from structural peculiarities, such as a more or less heterodispersed, sponge-like structure, while such interference does to a certain extent occur in many inorganic colloids such as silicates or phosphates. As a matter of fact, more complicated and varying conditions are prevailing here than in humus.

The more the ultramicron is structurally heterodispersed, the more difficult becomes the interpretation of the ionic exchange. An ion with small apparent effective volume disposes of a greater ion exchanging surface than a big ion having no access to all the inner surfaces. Thus small, slightly hydrated ions of low valence are favoured, if the ion exchanging substance possesses such a fine sponge structure that the big ions are unable to penetrate into every cavity. In low concentrations, 0.001 N. in figure 9, a big but polyvalent ion, for instance La or Ba, can replace more H-ions

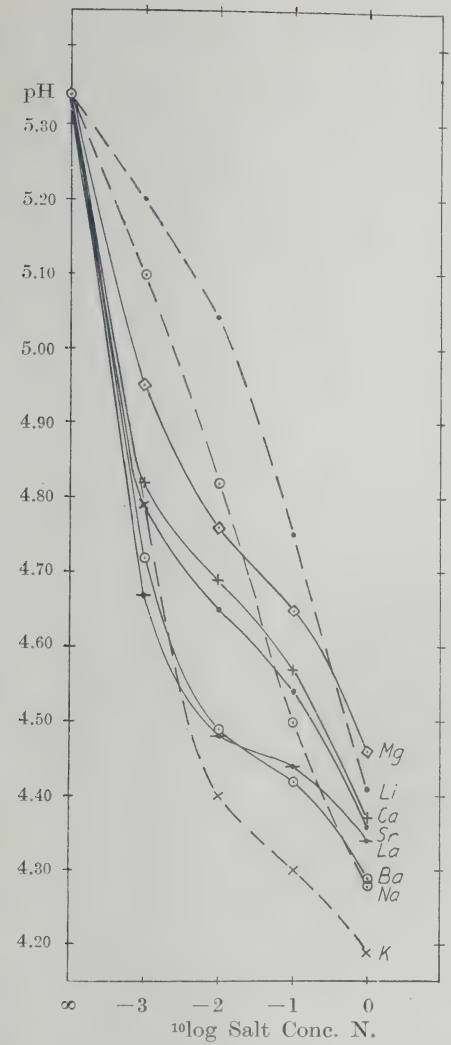


Fig. 9. Aluminium silicate I. pH series the same as in fig. 7.

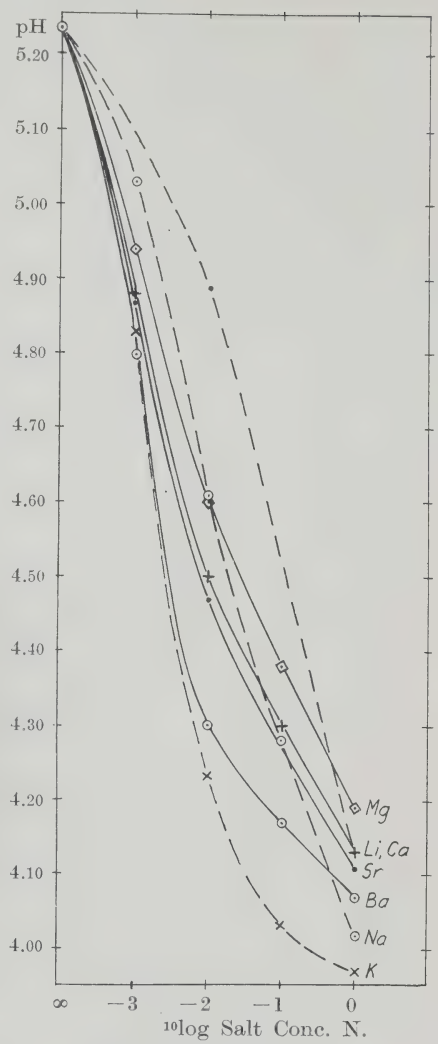


Fig. 10. Aluminium silicate II. pH series the same as in fig. 7.

than a little ion of low valence, for instance K. Certainly, the K-ion has a greater surface at its disposal but this is compensated by the stronger replacing power of the polyvalent ion. At high concentrations the number of H-ions to be found on the outer surfaces decreases to such an extent that a big, polyvalent ion, in spite of its greater replacing power, is unable to keep pace with a small ion which may

have a several times greater number of exchangeable H-ions at its disposal. The size and uniformity of the cavities and the ratio between outer and inner surfaces will at least in a certain degree be decisive for the relative pH-reducing effect and the replacing power of the ions. However, the ion blockade will not suffice as a satisfactory explanation of the »abnormal» exchange conditions. There may be reactions of an unknown nature, specific reactions, causing the exchange to deviate from those in an »ideal» acidoid. As will be shown below, these specific reactions are intimately connected with low pH-values. A thorough study of these problems must certainly be combined with an examination of the structure of the exchangers and an analysis of all ions in solution; this is however beyond the scope of the present investigation.

An experiment by Damsgaard-Sørensen (1941) indicates the influence exerted by the structure on the ion exchange. He leached NH_4-saturated permutite-G with calcium chloride solution. Here it proved very difficult to remove the last 20 % of the NH_4-ions. This was easily performed by KCl and NaCl, and also $BaCl_2$ replaced much better than $CaCl_2$. It is evident that the different efficiency of the replacing ions is not in agreement with their normal replacing power, which lies in the order: $Na < K < Ca < Ba$. An interfering effect of a high H-ion concentration is not to be expected here, since the permutite was treated with neutral salts. It seems to me that the phenomenon is connected with ion blockade.

The explanation might, at least partly, be found in the fact that Ca, having the greatest volume in the hydrated condition, shows the greatest blockade effect; next comes Ba, then Na and last K which also replaced most quickly.

From a purely theoretical point of view, even a big ion showing the blockade effect should be able to replace a smaller ion, provided that washing with the replacing ion is continued sufficiently long. On account of the decrease in concentration of the smaller ion on the outer surfaces, a slow outward diffusion from the inner surfaces will go on. But since the big ions are unable to »enter», the ions diffusing outward are replaced by H-ions from the water. A hydrolysis takes place. In such a case the ion swarm will contain more H-ions in the inner parts than in the outer ones.

Al-silicate II.

Similar pH-series as in the preceding case have been made. Since the glass electrode was used and the suspension effect was very strong, centrifugation was carried out and pH determined in the clear centrifugate. The results are given in figure 10.

As shown by the figure, the results closely agree with those found for Al-silicate I, the same commentaries being valid on the whole.

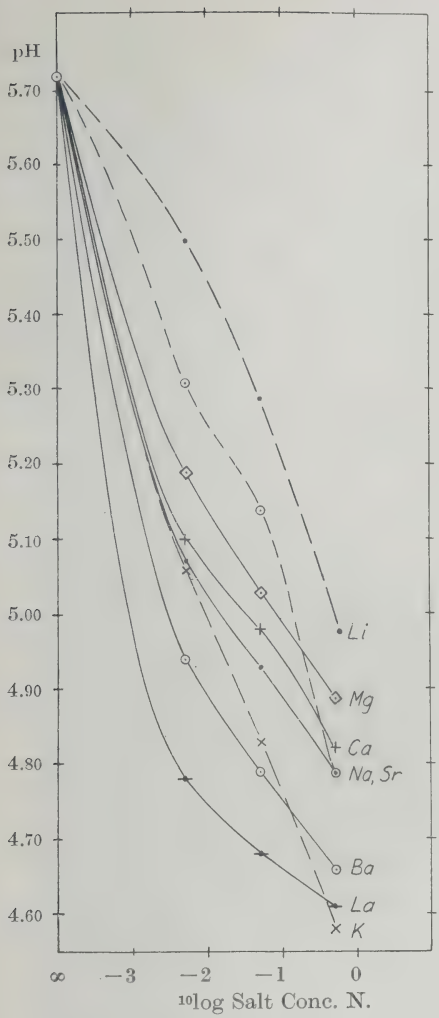


Fig. 11. Aluminium silicate III. Not dried after precipitation. pH in the same solutions as in fig. 5.

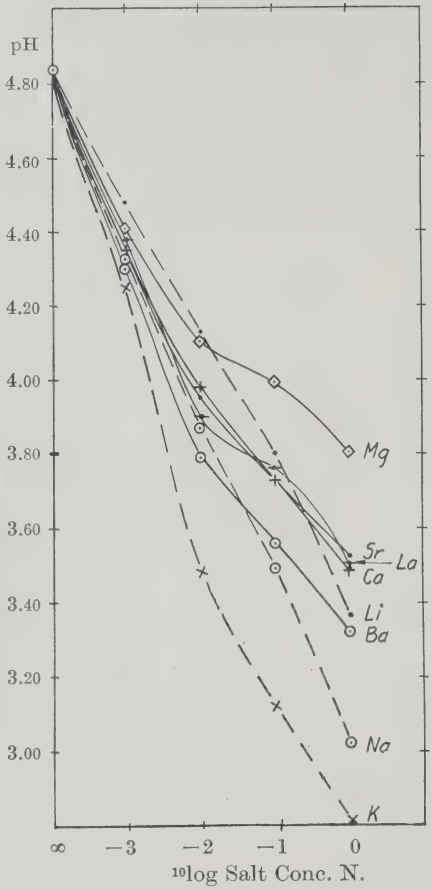


Fig. 12. Ferrisilicate. pH series and amount of substance the same as in fig. 5.

Al-silicate III.

With this silicate which had been precipitated »isoelectrically» but not allowed to dry, similar pH-series were made as for the other silicates. It was intended to find out, if there is a difference as to the exchange conditions between a dried silicate and a fresh silicate gel. The drying is likely to lead to an alteration of the structure,

implying a more complete development of a lattice structure and the formation of polyons by the union of monons whereby the inner surface grows at the expense of the outer surface and the blockade effect becomes more marked.

As pointed out before, the difference in composition between silicates I and III is relatively insignificant. The $SiO_2 : Al_2O_3$ ratio is 2.73 for the former and 2.22 for the latter; this disparity will scarcely have caused any greater difference in the exchange conditions.

The gel had a creamy consistency. After stirring it could be measured with the aid of a special pipette. 10 ml of the gel were mixed with 10 ml salt solution. pH was determined in the centrifugate and with the glass electrode. The results are shown in figure 11.

When figure 11 is compared with figures 9 and 10 a great difference is to be found between the relative position of the curves. The drying has apparently led to a considerable change of the ion exchange properties of the silicate.

The pH-reducing effect at 0.005 and 0.05 N. has the following order: $Li < Na < Mg < Ca < Sr < K < Ba < La$. Note the great disparity between K, Ba and La in the different silicates. Only at the highest concentrations in silicate III the K-curve intersects the Ba- and La-curves. The normal valence effect could manifest itself more strongly here than in the silicates I and II.

The valence effect was still more marked in an experiment made by Bacon (1936), who found pronounced dissimilarities between different valence groups with regard to the pH-reducing effect. To newly precipitated and not dried aluminium-silicate gel 0.1 N. solutions of nitrates and chlorides were added whereafter pH was determined. The pH was reduced in the following order: $Na \leqq K < Ca = Ba < La$.

The divergences of the ion exchange existing between silicate III and Bacon's silicate gel, may be due to differences in the structure and composition of the gels and to the fact that the pH-values in Bacon's experiment lay between 6.39 and 5.58.

Ferrisilicate.

The results from the pH-series — glass electrode — are to be found in figure 12.

It appears from the figure that the alkali ions reduce the pH very strongly as compared with polyvalent ions. Already in 0.001 N. solution, K reduces the pH-value more than Ba does. At the highest concentrations, the order is: $Mg < Sr \leqq La \leqq Ca < Li < Ba < Na < K$.

K lies particularly low. Even Li nearly equals Ba in 1.0 N. solution. The entire La-curve lies very high.

At present, it is impossible to decide to what an extent these great deviations from the exchange conditions in an »ideal» acidoid may

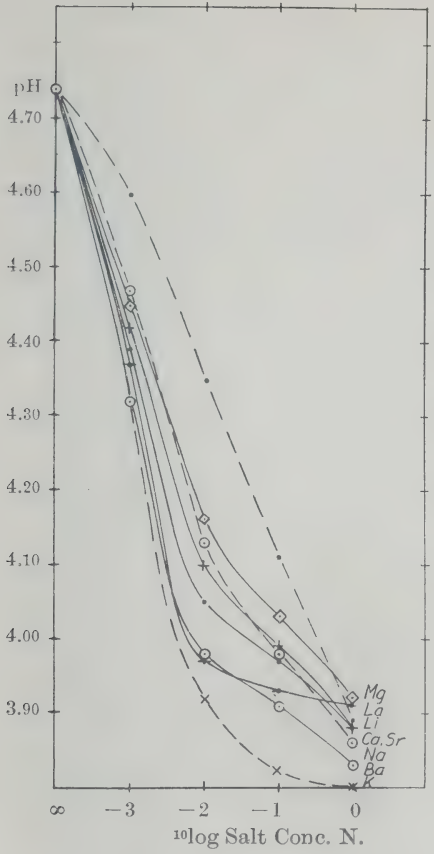


Fig. 13. Permutite. pH series as in fig. 7.

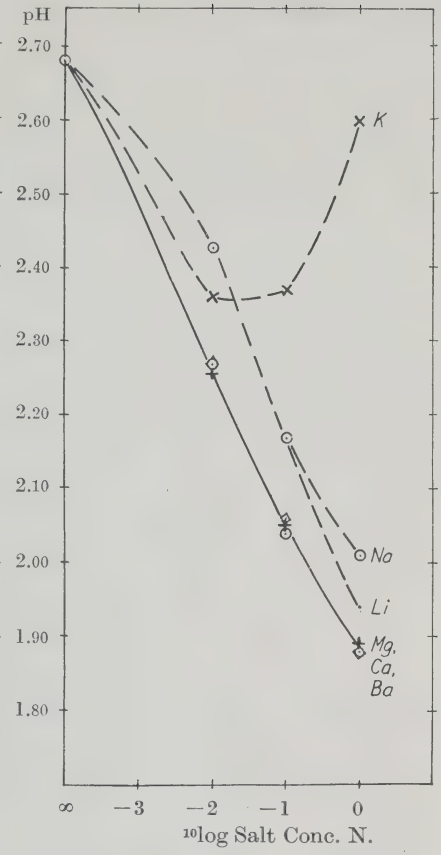


Fig. 14. Bentonite. pH series as in fig. 7, Sr and La excluded.

be traced back to ion blockade. Undoubtedly, ion blockade plays a certain rôle but other, so far unknown factors may be imagined to be of great importance. In the suspensions of 0.1 and 1.0 N. NaCl and $CaCl_2$ dissolved Fe was estimated with thiocyanate. However, no trace of Fe could be detected.

Permutite.

Permutite is a technical product consisting of aluminium silicate and, as mentioned before, possesses a spongy structure and usually a high cation exchange capactiy. According to HOFMANN (1942) and others, permutite is to be considered as an amorphous substance.

The results from the pH-series appear in figure 13.

The pH has been decreased in the order:

at 0.01 N.: $Li < Mg < Na < Ca < Sr < Ba \leqq La < K$

at 1.0 N.: $Mg \leqq La < Li \leqq Ca = Sr < Na < Ba < K$.

The order within every valence group agrees with the lyotropic series but, for the rest, the position between the different ions is scarcely dependent on the valence. La, especially, seems to decrease the pH slightly at high concentrations. The ion exchange conditions of permutite are similar to those of the dried silicates treated above, so that no additional explanations are needed.

In order to find out if the relative position of the K- and Ba-curves changes with the length of the time of reaction, pH in 0.1 N. solution was taken 13 days after the addition of the salt. The difference in pH between KCl and $BaCl_2$ was 0.08. Figure 13 shows that the corresponding difference amounts to 0.09. It appears from this that a long time of reaction does not change the result.

Damsgaard-Sørensen (1941) found the following cation exchange capacities for a permutite-G (calculated by the author to the weight of H-saturated material):

	Na	NH_4	K	Ba
m.e./g	2.07	2.184	2.21	2.17

This result being in analogy with the pH-values obtained with the silicates I and II in 0.1 N. solution and, to a certain extent, also with those obtained with permutite, compare figures 9, 10 and 13, evidently points at the importance of the structure for the ion exchange. A possible disturbing effect of a high H-ion concentration is not to be expected here, as the exchange capacity is determined at pH 7.

In the introduction, some of Jenny's (1927) exchange experiments with permutite have been related. As it appears his results are in rather good agreement with my own observations.

Bentonite.

Bentonite is a clay the origin of which is problematical. Its main component is the mineral montmorillonite, $Al_2O_3 \cdot 4\ SiO_2 \cdot H_2O + nH_2O$. The crystalline structure, swelling in water, and pronounced inner surface ion exchange have been dealt with before. According to Mattson (1932), no amphoteric character is indicated by the reactions of bentonite neither electrophoretically nor by its exchange reactions. Mattson even believes that bentonite must be considered to be a stronger acid than humus. Its cation exchange capacity varies between 80 and 100 m.e./100 g.

pH-series as before have been made with H-bentonite; however, 0.001 N. has been omitted. Figure 14.

The following results appear from the figure:

1. The bivalent ions, throughout, reduce pH in a higher degree than the monovalent ones. This effect may appear unexpected since bentonite is a silicate and the silicates in earlier cases behaved in a different way. The explanation may be found in the fact that no ion blockade occurs here but that ionic exchange takes place unimpeded within the open lattice of bentonite allowing the »normal» adsorption of the ions.
2. Mg, Ca and Ba replace with the same strength at all concentrations.
3. Na and Li replace with equal strength except in 1.0 N. solution where Li is stronger than Na. The same was the case in humus, the reason being presumably the same. Like humus, the H-bentonite may have a rather high inside concentration making possible such an effect if the difference $f_{Li}—f_{Na}$ as well as f_H in the outside solution rapidly grow.
4. The K-curve exhibits a strange course which, at present, cannot be explained satisfactorily. Specific conditions must be assumed to prevail here giving rise to this strange reaction. The determinations have been repeated without a change in the results. For the rest, KCl behaves in the same way in the bleaching earths which are closely related to bentonite, figure 15. The anomaly of potassium chloride in montmorillonite will later be studied more closely.

Regarding the relative replacing power of Li and Na in 0.01 N. and 0.1 N. solution as well as that of Mg, Ca and Ba in all concentrations, the results are in agreement with those of SCHACHTSCHABEL (1940). He found that, when ion exchange took place between NH_4-montmorillonite and alkali and alkaline-earth chlorides, the difference between Li and Na was minute and that Mg, Ca and Ba were adsorbed practically to the same extent. The alkaline-earth ions replaced more strongly than Li, Na and K. It is of interest that KCl behaved »normally» towards NH_4-montmorillonite.

Kaolinite.

The main constituent of kaolin or porcelain-clay is the mineral kaolinite with the composition: $Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$. The structure of kaolinite has been dealt with before. As mentioned above, kaolinite performs only outer-surface ion exchange and its base exchange capacity is very low. It will be seen from the neutralization curve, figure 20, that in 0.1 N. salt solution it binds only about 3 m.e./100 g at pH 7. On account of the low cation exchange capacity of kaolinite and because the reactions presumably took place too close to the equi-ionic point, the exchange acidity was low and the difference between the ions somewhat uncertain. No numerical results from

these series are therefore presented. The neutralization curve will be published below. However, it shall be mentioned here that the pH-determinations gave no indication of ion blockade and that the replacing power had the order:

$$\text{monovalent} < \text{bivalent} < \text{trivalent},$$

although the differences were minute.

Bleaching earths.

For the bleaching of oils certain clays of natural occurrence are used at present, which are made active by treatment with H_2SO_4 or HCl. According to HOFMANN, ENDELL and WILM (1934), the bleaching earths have the same composition and structure as bentonite; thus, they possess a montmorillonite-structure. Since it is of interest to compare ionic exchange in these unique clays with other colloid material, especially bentonite, they have been included in the experiments. However, concentration series have only been executed with K- and Ba-chloride. The cation exchange capacity, determined after CHAPMAN and KELLEY (1930), was for German bleaching earth 1, activated with H_2SO_4, 56 and for German bleaching earth 2, activated with HCl, 52 m.e./100 g.

The results of the determinations are presented in figure 15.

It appears that the bleaching earths behave like bentonite as could be expected on account of their likeness as to the mineral composition. pH has also been determined in 1.0 N. solution of the cations not included above, whereby results corresponding to those for bentonite were obtained, table 5.

Table 5. *Determination of the pH-value of electrodialysed bleaching earths.*

Soil	In 1.0 N. solution of						
	NaCl	KCl	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	$LaCl_3$
German bleaching earth 1	2.19	2.49	—	2.12	—	2.15	2.14
German bleaching earth 2	2.20	2.60	2.13	2.13	2.15	2.15	2.17

The strange behaviour of the bleaching earths and the bentonite in KCl-solution might be imagined to be due to a reaction requiring time. In order to investigate this, pH was determined for the German bleaching earth 2 in 1.0 N. solution after 1/60, 2, 15 and 24 hours' time of reaction. The result indicated, however, that the reaction was very rapid, as all the pH-values were the same within the range of the experimental error.

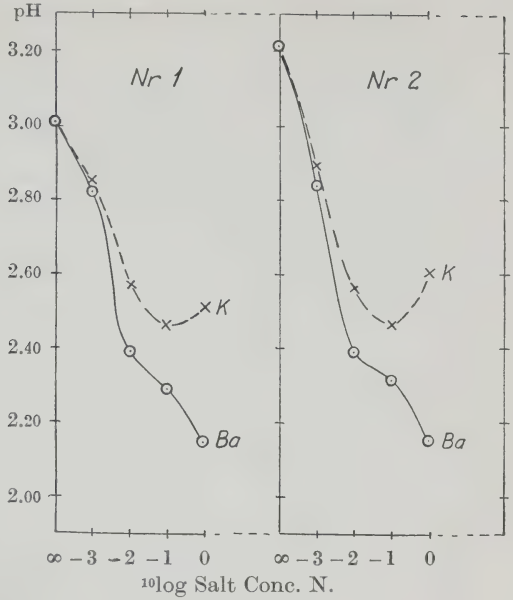


Fig. 15. German bleaching earths. Nr. 1 activated with H_2SO_4 and 2 with HCl. pH in K- and Ba-chlorides. 1.0 g in 10.0 ml solution.

The frequently applied method to determine the pH of a soil in 1.0 N. KCl gives constant and reliable values in most cases. But, as appears from the determinations in bentonite and the bleaching earths, results may be obtained which do not express the conditions in other salt solutions and yield too low values for the acidoid activity of the soil. From this point of view, a comparative investigation of a greater number of soils containing montmorillonite seems to be justified.

Mineral soils.

pH-determinations were made in 0.1 N. solutions for the soils named in the list of materials. 4.0 g soil in 10.0 ml solution. Table 6.

Table 6. *Determination of the pH-value of electrodialysed soils in 0.1 N. salt solutions.*

	Water	LiCl	NaCl	KCl	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	$LaCl_3$
Soil from Sperlingsholm	3.94	(3.10)	3.15	3.11	3.06	3.03	3.05	3.01	2.85
Soil from Fristorp	3.80	3.17	3.17	3.13	3.11	3.10	3.11	3.06	3.01
Soil from Kungsängen	3.97	3.17	3.18	3.15	3.11	3.10	3.11	3.10	3.03
Ancylus clay from Ärna	4.58	3.80	3.75	3.44	3.54	3.49	3.49	3.44	3.35

The following appears from the table:

1. The ions of the different valence-groups reduce the pH-value in the following order: monovalent < bivalent < trivalent.

2. The differences between the groups and between the ions within the groups are small. Throughout, the K- and Ba-ions reduce the pH-value more than the other ions within the respective groups, but the difference is insignificant.

3. The Ancylus clay behaves somewhat differently from the other soils by yielding the following order: Li < Na < Mg < Ca = = Sr < K = Ba < La.

It is difficult to explain this divergent behaviour of the Ancylus clay. It is possible that the Ancylus clay has a composition different from the other soils as to the clay minerals. As shown by SCHACHTSCHABEL (1940) the K- and NH_4-ions have a strong sorption tendency towards minerals of the mica type. Consequently, a higher content of mica in the Ancylus clay may have caused the K-ion to reduce the pH-value relatively more strongly in this material than in the others. Unfortunately the contents of the Swedish soils of the different clay minerals have not been the subject of any investigation, so that no indication as to the interpretation of the present question can be found in that way.

4. The values obtained are, except for K in Ancylus clay, in agreement with the results of TERÄSVUORI and ARRHENIUS. As mentioned before, these investigators found that in soils the pH-value was reduced in the order: Na < K < Mg < Ca. However, for that reason one may surely not expect that all soils would behave in the same way towards added neutral salts, though the deviations from the conditions in an »ideal» acidoid rarely will be as great as in certain of the synthetic ion exchangers.

B. *Neutralization curves.*

It followed from the concentration series that the relative pH-reducing effect and replacing power of the cations — as indicated by the pH — varied in a high degree in accordance with both the nature of the ion exchanging substance and the concentration of the salt. No information has been gained, on the other hand, whether the mutual order of the ions changes with the pH in the suspension. This information, however, is given by the neutralization curve. To bring out this relationship it was not considered necessary to include all salts used before; therefore only NaCl, KCl, $CaCl_2$, and $BaCl_2$ have been used. $LaCl_3$ is hydrolysed at higher pH and has therefore been omitted. Moreover, only part of the investigated materials have been included here.

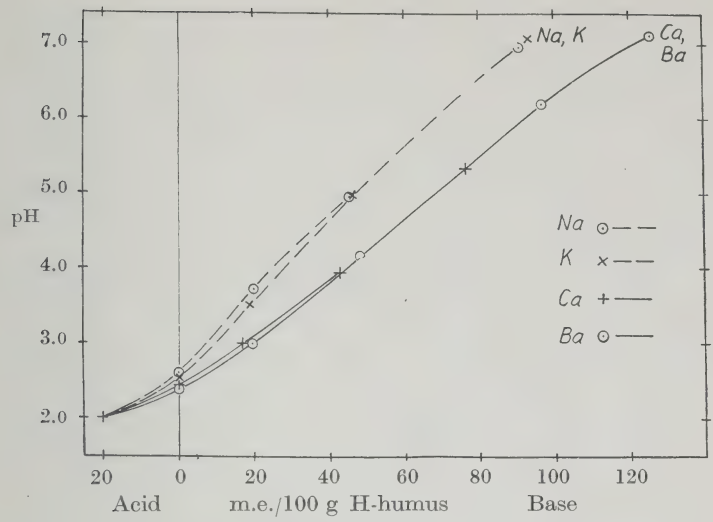


Fig. 16. Neutralization curves in 0.1 N. Na-, K-, Ca- and Ba-chlorides of humus from Häggbygget F_2. 1.000 g substance in 20.0 ml solution.

The material was weighed into pH-tubes whereafter the calculated amounts of water, salt solution, and hydroxyde were added in that order. Throughout, the salt concentration has been 0.10 N. The time of reaction has been the same as in the concentration series.

Humus from Häggbygget.

The results are presented in figure 16.

On account of the low solubility of the calcium hydroxyde it has not been possible to reach higher values than a little above pH 5 for the Ca-curve.

It appears from the figure that the replacing power of the Ca- and Ba-ions in relation to that of the Na- and K-ions increases considerably with increasing pH. This becomes evident by a widening of the horizontal distance between the neutralization curves.

In salt solutions without addition of either acid or base a certain difference between the pH-reducing power of the ions is to be found, but this difference is not constant and not independent of the pH of the outside solution. This is explained as follows:

If the replacing power of a monovalent ion is a certain fraction of that of a bivalent ion, the difference between the total number of H-ions replaced from an acidoid by the bivalent and by the monovalent cations must develop from zero (at low pH) towards a maximum and back again to zero, in accordance with the increase

in the pH-value and the growing degree of protolysis. Both for »ideal» and real weak acidoids the neutralization curves will not be fully symmetrical since the apparent dissociation constants grow somewhat during the titration, and this increase is greater for the bivalent ion than for the monovalent one. The vertical distance between the neutralization curves will therefore be greater in the upper part ($pH > pk$) of the curves than in the lower ($pH < pk$). The curve of the bivalent ion will, in its lower and medium part, show a weaker incline than the curve of the monovalent ion.

These conditions are governed by the activity coefficients and their variation and the z-value in the Donnan formula. When acid is added, the degree of protolysation decreases and with this the z-value and the ionic strength of the colloid ion. When the acidoid is neutralized, the degree of protolysation, the z-value, and the ionic strength increase. The concentration of the outside solution is, however, practically constant while the neutralization is in progress, so that even the activity coefficients of the ions in the outside solutions may be considered as being constant. In the inside solution, on the contrary, the activity coefficients decrease when the acidoid is neutralized, the change being greater for the bivalent than for the monovalent ions. On account of the growing ratio $z : x$ the valence effect (cf. part II:10) increases with the neutralization degree. It appears from what has been said that, when an acidoid is neutralized, the ratio between the replacing power of a bivalent and a monovalent ion must, within certain limits, grow symbatically with the pH and thus cause asymmetrical neutralization curves even for an »ideal» acidoid.

Ferrisilicate.

The results are given in figure 17.
The figure shows:

1. At the 0-point of the abscissa the cations reduce the pH-value in the order: $Ca < Ba < Na < K$; but as pH grows, the Ba- and Ca-curves approach the curves of the monovalent ions and finally intersect them. Thus, at the highest pH-values the »normal» order is established: $Na < K < Ca < Ba$. Consequently, the strong deviation of the Fe-silicate from the behaviour of an »ideal» exchanger and that of humus, which was in the first place considered as a result of specific reactions, seems to be connected with the pH of the suspension. At low pH the deviation in the relative order of the pH-reducing power of the ions is great, but with increasing pH the deviation decreases and finally disappears.

2. When compared with each other the Na- and K-curves are found to be in agreement with the theory. The same applies for the Ca- and Ba-curves.

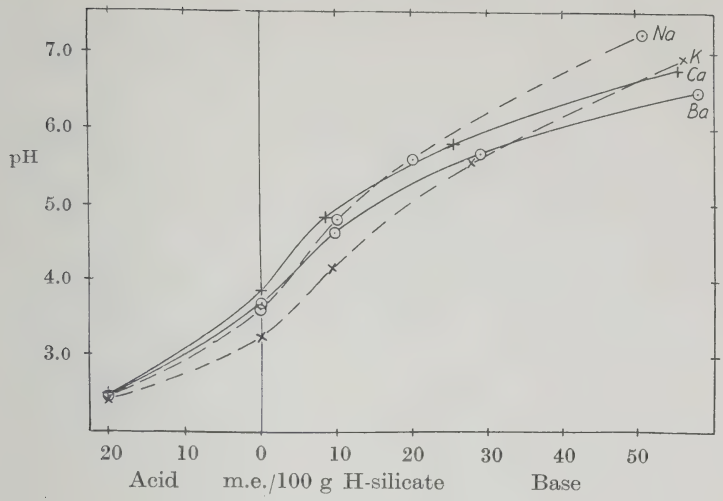


Fig. 17. Ferrisilicate. Neutralization curves as in fig. 16.

Permutite.

The results are to be found in figure 18.

By comparing figure 18 with figure 17 it will be seen that permutite and ferrisilicate behave in a similar way. What was said about ferrisilicate is apparently also valid here.

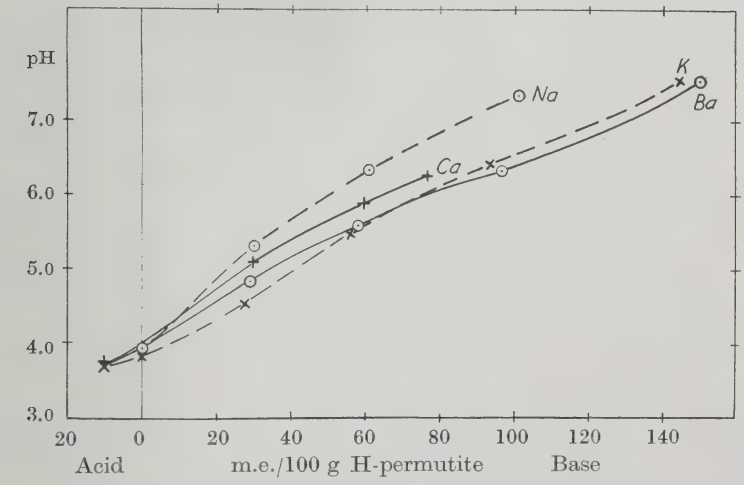


Fig. 18. Permutite. Neutralization curves as in fig. 16.

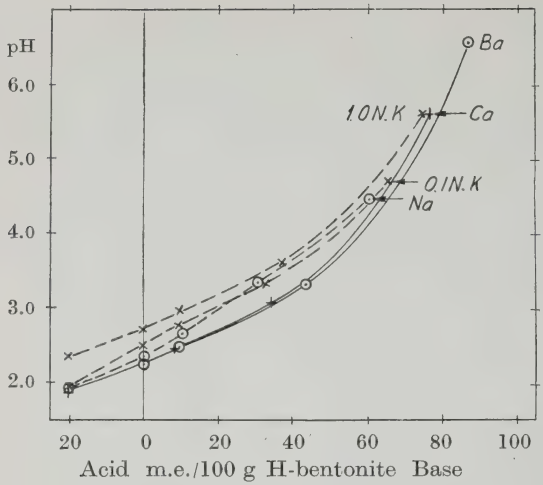


Fig. 19. Bentonite. Neutralization curves in 0.1 and 1.0 N. KCl and in 0.1 N. Na-, Ca- and Ba-chlorides. 1.000 g substance in 20.0 ml solution.

Bentonite.

As appeared from figure 14, bentonite yielded considerably higher pH-values in 1.0 N. than in 0.1 N. KCl. However, these strange conditions could not be explained. In order to find out if the distance between the two KCl-curves varies with the pH-value, both 0.1 N. and 1.0 N. KCl were included in the neutralization curves. Figure 19.

The following appears from the figure:

1. The distance between the pH-curves for 1.0 N. and 0.1 N. KCl is considerably greater at the lowest pH-value than at the higher ones where the distance is rather constant. The curves should have been continued to higher pH-values but unfortunately there was not sufficient material. Still the conclusion may be drawn that the strange reaction of potassium chloride with bentonite is not to any greater extent dependent on the hydrogen ion concentration but seems to decrease somewhat with growing pH-value.

2. In agreement with the concentration series, the Na-curve in 0.1 N. solution lies at low pH below the K-curve. But already at a pH of about 3.1 the curves intersect whereafter K lies below.

3. At low pH-values the Ca- and Ba-curves coincide but, with increasing pH, the curves diverge in agreement with the theory.

Kaolinite.

On account of the very low cation exchange capacity of kaolinite, 2 g/20 ml were used for the neutralization curves. All curves running very closely together, only those of KCl and $BaCl_2$ were included in figure 20.

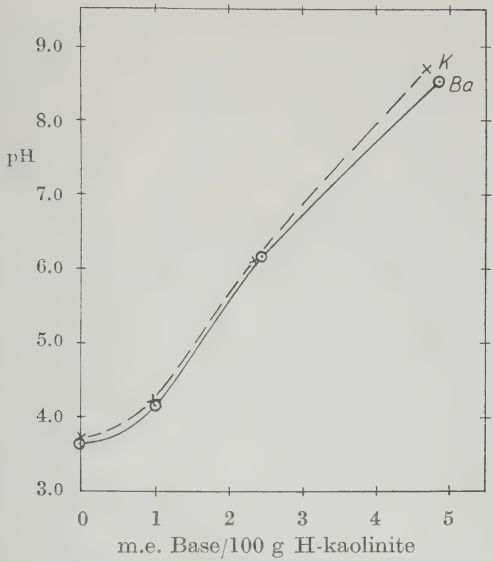


Fig. 20. Kaolinite. Neutralization curves in 0.1 N. KCl and $BaCl_2$. 2.000 g substance in 20 ml solution.

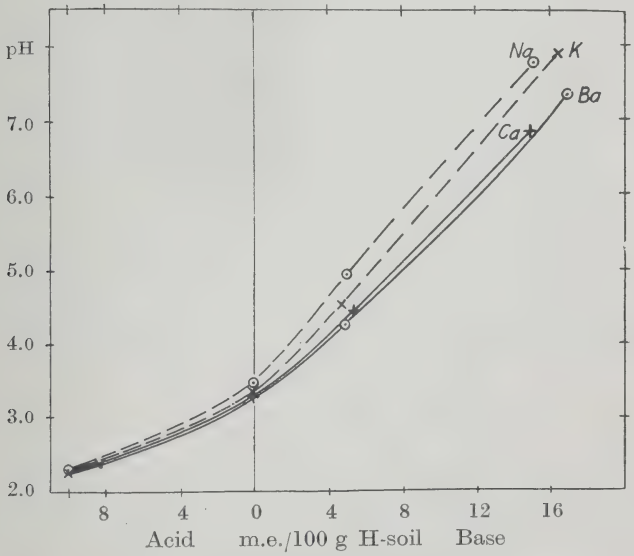


Fig. 21. Surface soil from Sperlingsholm. Neutralization curves in 0.1 N. NaCl, KCl, $CaCl_2$ and $BaCl_2$. 2.000 g substance in 20.0 ml solution.

There is only little difference between K and Ba, but it clearly appears that Ba is more strongly replacing, especially at higher pH. Considering the fact that ionic exchange here only takes place on outside surfaces, this result was to be expected. Compare the conditions in humus from Häggbygget F_2.

Surface Soil from Sperlingsholm.

The results appear from figure 21.

In conformity with humus and kaolinite the Sperlingsholm soil behaves »normally» the order for the replacing power over the whole pH range being: $Na < K < Ca < Ba$.

The neutralization curves of the different materials seem to justify the conclusion that the relative pH-decreasing power of cations is at low pH-values in the first place determined by the nature of the exchanger and at higher pH-values generally by the kind of the ions and the strength and exchanging capacity of the acidoid.

7. Conclusions.

It has been shown theoretically that in an »ideal» acidoid the replacing power and the pH-reducing effect of the cations are determined by:

1. the activity coefficient of the ions. The lower this is in the micellar solution, the stronger the replacing power. The activity coefficient is a function of the valence, the effective diameter of the hydrated ion, the protolysation degree and the exchange capacity of the acidoid (ionic strength of the micellar solution), and the concentration of the salt added.

2. the »relative dilution», i.e. the ratio between the activity of the inside and outside solutions. The greater this ratio, the stronger is the replacing effect exerted by a polyvalent ion compared with a monovalent. The theoretical considerations have led to the result that the following ions may be arranged according to their replacing power and pH-decreasing effect in the order:

$$Li < Na < K < Mg < Ca < Sr < Ba < La.$$

This order is valid in an »ideal» acidoid and in a true acidoid where the structure raises no impediments for the diffusion of the ions to and from the exchanging groups. In a great number of exchanging materials, however, greater or smaller deviations from the above order are to be found. The experimental results indicate that the relative pH-reducing power of cations is determined by:

1. the nature of the ions,
2. the nature of the exchange material,
3. the concentration of the added salt,
4. the pH of the suspension.

The organic material was found, in the connections treated here, to behave like an ideal acidoid, since the pH-decreasing power of the ions in concentrations up to 0.1 N. agreed with the order given above. In 1.0 N. solution the order was reversed for the alkaline ions: $K < Na < Li$, while it remained unchanged both for the other ions and between the valence groups.

In the inorganic material the order varied considerably, both from one substance to the other and with the salt concentration. At higher concentrations (0.1—1.0 N.) the alkali ions as a rule decreased the pH more strongly than the corresponding alkaline-earth ions. This has been considered to be caused partly by ion blockade due to structural peculiarities and partly by specific reactions.

The neutralization curves showed that an inversion of the mutual order of the pH-decreasing power of the ions may occur as the pH increases. The »normal» adsorption energy of the ions proves more effective at higher than at lower pH-values. Therefore, the importance of the nature of the ion exchanger seems to decrease with growing degree of protolysation.

As shown by the investigation, it is not possible to obtain a general relative order of the pH-reducing power of the more common alkali and alkaline-earth ions and the lanthanum ion. The same is undoubtedly the case even for the other ions. Therefore, it is evidently meaningless and often misleading to advance such a series without, at the same time, mentioning the type of the exchanger and the concentration of the replacing ions.

IV. General Properties of a Resin Acidoid and Basoid.

1. Introduction.

Because of the great importance of synthetic-resin ion exchangers for, among other things, the technique of water softening and desalting and for analytical chemistry, and because of the fact that such a resin, *Wofatit K*, is extensively used in the following investigations, the general properties of this cation exchanging material shall

be studied here more closely. This seems to be the more justified as it has proved impossible to secure all the information desired about the properties of synthetic resins which are of importance from the point of view of ionic exchange. On the other hand, the description of the anion exchange resin, *Wofatit M*, has been given in a more summary way, partly because anionic exchange has been studied in the following to a minor extent than cation exchange, and partly because anion exchangers so far do not seem to have the same importance for technical purposes as cation exchangers. A general survey of the synthetic resins is given by Myers (1942).

2. The Cation Exchange Resin Wofatit K.

Wofatit K belongs to the great number of synthetic ion exchangers produced by I. G. Farbenindustrie A.-G. and known in Sweden under the common name of organolites. According to Griessbach (1939) Wofatit K is a condensation product of acidic, aromatic compounds (phenols) with formaldehyde, and according to the same investigator it is a pure cation exchanger, the ionogen groups of which consist of aromatic nuclear-sulphonic-acid groups ($-SO_3H$) distributed within the homogeneous resin gel of an almost lattice-like structure. Sulphonic acids being strong acids, Wofatit K in aqueous solution may be considered as being completely protolysed. Neutralization curves which were made for resins by Griessbach (1939) and Richter (1939) confirm this assumption. Samuelson (1944) has studied similar sulphonic ion exchangers, some of them produced by himself, and especially their application in the chemical analysis.

Apart from the properties mentioned of Wofatit K, it may be added that resins are said to be insoluble in water and salt solutions and, as far as cation exchangers are concerned, to be very insensible to strongly acidic solutions and to possess both high reaction velocity and exchange capacity.

The resin contained some big grains and was therefore sifted through a 2 mm sieve. The Na-saturated resin was treated at first with 2 N. and then with 0.5 N. HCl until all Na-ions were replaced by H-ions. By this treatment the small amounts of HCl-soluble iron compounds contained in the resin were removed at the same time. The dissolution of the iron was controlled by testing as to trivalent iron with potassium ferrocyanide. After some washings the iron reaction had completely disappeared. The resin was freed from chloride by washing with distilled water and then dried at 30—35° C. The contents of dry matter were determined in the vacuum above P_2O_5 at room temperature.

A. *Contents of S, Fe, and N.*

S and Fe were determined by burning 500 mg resin with sodium peroxide (Na_2O_2) in the peroxide bombcalorimeter of PARR. By this the sulphur is oxidized into sulphate. The melt was dissolved in water, and the solution was acidified with HCl. The iron was then precipitated with NH_3 and titrated with $KMnO_4$. In the filtrate from the iron determination the sulphate was determined by precipitation as $BaSO_4$ according to HILLEBRAND and LUNDELL (1929). The nitrogen was determined by the KJELDAHL procedure. Table 7 gives the results from the analyses; the N content of Wofatit M is given in the same table.

Table 7. *Analysis of H-Wofatit K as to S, Fe and N and of OH-Wofatit M as to N, calculated in per cent of the dry matter.*

	S	Fe	N
H-Wofatit K	7.64	0.36	0.03
OH-Wofatit M	—	—	18.30

In spite of the intensive washing with hydrochloric acid, the resin still holds some iron which, however, must be assumed to be in a nonexchangeable form.

B. *Time necessary for wetting.*

Certain materials, for instance humus, seem to hold a layer of air so strongly adsorbed that wetting by water is delayed. The same might be thought to be the case in resin, perhaps to a still higher degree on account of the capillary structure and the extremely large inner surfaces of the resin grain. Therefore, if such a substance as resin is to be used for ionic exchange, it is of interest to know how quickly the moistening process is performed. The ion exchanging capacity cannot be considered to be maximal unless the inner surface has become completely wetted.

The velocity of moistening has been studied by determining the specific gravity of the resin with the aid of the volume-pycnometer of OSTWALD at different times after water had been added. While the wetting is going on, the specific gravity will increase, but finally, become constant when the resin is completely soaked. 20.000 g of the air-dried substance were weighed into pycnometer flasks, and sufficient distilled water was added to cover the resin. The flasks were then placed in a slow shaker. The specific gravity was determined after 1, 24 and 120 hours respectively. The determinations were made at thoroughly controlled temperature. For comparison a determination was made by evacuation. After water had been

Table 8. *The specific gravity of H-Wofatit K, with and without evacuation.*

	Without evacuation				With evacuation
Hours after addition of water	1	24	120	120	17
Specific gravity	1.6701	1.6771	1.6799	1.6800	1.6801

added, the pycnometer was placed into a desiccator and slowly evacuated. The pycnometer was kept for 5 hours in the vacuum and after that for 12 hours without vacuum.

It appears from table 8 that the specific gravity grows but slowly without evacuation, but after 120 hours it has reached the same value as with evacuation. Evidently the resin should either be moistened in advance or the time of reaction has to be taken rather long.

C. *Solubility in water.*

For analytic purposes it is recommended to use cation exchange resins in a H-saturated state for the separation of cations and anions (Samuelson 1942 a). The cations are quantitatively exchanged for H-ions. After the solution which is to be analysed has passed through, the adsorbent is washed until the filtrate becomes neutral. The released amount of acid which is equivalent to the cations adsorbed, may then be titrated in the ordinary way. The method is only applicable on condition that the ion exchanger does not release any traceable amounts of acidic substances (for instance by loss of sulphonic-acid groups caused by hydrolysis) or, if this should be the case, that it is a question of so low amounts that a correction can be introduced.

11.0 g of air-dried H-resin were put into a suitable apparatus (a vertical tube furnished with a stopcock below and a container for the liquid above) and soaked for several days. The resin column was 12 cm long and 1.3 cm in diameter. 1000 ml of distilled water, which was freed from carbon dioxide, were allowed to run through the column at the rate of 22 ml per minute. The effluent was evaporated until 50 ml were left and titrated with potassium hydroxide, a mixture of methyl red (MR) and methylene blue (MBl) being used as indicator. The addition of $BaCl_2$ showed no trace of a precipitate. In the same beaker 1 liter of distilled water, which was free from carbon dioxide, was evaporated until 50 ml were left and titrated in the way described above. This titration value was considered as a blank and was subtracted. Calculated per one gram of P_2O_5-

Table 9. *Titration of acids dissolved by the shaking of H-Wofatit K in water. m.e./g dry H-Wofatit.*

Time of shaking, hours	Rotating shaking machine		Shaking machine working horizontally
	1	24	1
Strong acids	0.056	0.091	0.052
Weak »	0.010	0.011	0.009

dried H-resin and per 100 ml of the filtrate, acidic substances to the amount of 0.000070 m.e. were solved out.

By leaching with water an analytically demonstrable amount of acid has apparently been dissolved. However, the quantity is so little that in not too minute analyses the error may be either neglected or corrected for.

D. *Mechanical stability in water.*

It is a general practice in ion exchange experiments to shake the ion exchanging material more or less thoroughly in order to attain the equilibrium as quickly as possible. When the exchanger has a grain structure, as is the case with Wofatit K, and when the mechanical stability is not very high, the shaking may result in the dissolution of part of the material in a mechanical way.

The following experiment was carried out: 5.000 g of H-resin were weighed into flasks, 100 ml of distilled water, which was free from carbon dioxide, were added, whereafter shaking took place for 1 and 24 hours respectively in a rotating Wagner shaking-machine. For comparison, other samples were shaken for 1 hour in a shaking-machine moving forward and backward, by which mainly the fluid was heavily agitated. While the shaking was going on, the flasks were also shaken by hand several times in the latter case. The solution was filtered through a membrane-filter (fine, size of pores 1 μ—50 mμ). 60 ml of the filtrate were titrated with sodium hydroxyde, at first, against MR, for strong acids and then, against phenolphtalein (PP), for weak acids.

In spite of the fact that the resin grains are hard and glassy, a not insignificant amount of acid has been dissolved by the shaking. The rotating machine has brought about a more intense solution. Judging from the result a proportionally greater amount is dissolved by a short shaking than by a long one. Among the acids solved the strong acids are dominating; therefore, it is most probable that it is a question of sulphonic-acid groups being released.

In the following ion exchange experiments the resin has as a rule been shaken partly in the horizontally working shaking-machine

and partly, now and then, by hand, but always as gently as possible. The dissolution which was observed leads to the effect that adsorbed ions are liberated and the exchange capacity, perhaps, decreases a little. However, this effect will not reach such a magnitude as to render doubtful or inaccurate the results achieved or the conclusions drawn from these.

E. *Time required for exchange equilibrium.*

The time necessary for attaining the exchange equilibrium with resins has been the subject of a number of investigations by, among others, WALTON (1943), SAMUELSON (1944), and NACHOD and WOOD (1944). They all agree that the equilibrium is reached quickly. Yet, there seem to be certain divergences on account of the kind of the resin used.

Two experiments have been made regarding the velocity of the reaction. In experiment nr. 1 the additional question was examined, to what an extent the time necessary for attaining the equilibrium is influenced by the length of the interval between the moistening of the resin and the beginning of the reaction.

Experiment nr. 1.

10.00 g of air-dried H-resin were weighed into two 1000 ml volumetric flasks. 250 ml of distilled water, which was free from carbon dioxide, were added in one of the flasks which was then kept for 10 days. The 250 ml of water were not added to the other flask until the ninth day. On the tenth day 20.00 m.e. NaCl and water up to the mark were added in both flasks which were then shaken in a Wagner machine for the times mentioned below. A sedimentation-time of five minutes is not included. 100 ml were titrated with NaOH, MR being used as indicator.

Table 10. *The time necessary for equilibrium between H-Wofatit K and NaCl, the resin being moistened either 1 or 10 days before the beginning of the reaction.*

Time of reaction, minutes	ml of 0.1034 N. NaOH used	
	1 day	10 days
10	10.58	10.65
20	10.79	10.84
40	10.84	10.88
80	10.86	10.89
160	10.87	10.89
70 hours with, and 17 hours without shaking	10.96	10.95

It appears that the ion exchange has progressed somewhat more slowly in the material that had been moistened only one day before the beginning of the reaction. The difference in the exchange acidity, however, is insignificant and amounts after 10 minutes hardly to 0.7 % and after 160 minutes it has practically disappeared. On the whole, ionic exchange has been accomplished quickly. Already 10 minutes after the addition of NaCl to the material that had been moistened for the longer period, 97.8 % of the exchange acidity to be found at the equilibrium were reached. After 40–80 minutes the equilibrium was attained. The slight increase of the exchange acidity after another 87 hours may be caused by the long-lasting shaking and ensuing mechanical action upon the resin grains.

Experiment nr. 2.

5.000 g of air-dried H-Wofatit K were weighed into five 300 ml Erlenmeyer-flasks, and a calculated amount of distilled water and 3.879 m.e. KOH were added whereafter shaking took place for four days. Thereafter 4.109 m.e. NH_4OH and 31.96 m.e. HCl were added. Σ KOH + NH_4OH = 205.0 m.e./100 g dry H-resin. HCl = 400 % of Σ m.e. K + NH_4. The total volume of the solution was 120 ml. After shaking for 1, 5, 24, 48, and 96 hours the solutions were filtered and the filtrates analysed in the way described above regarding the contents of NH_4.

Table 11. *The time necessary for attaining equilibrium of reaction between K-H-Wofatit K and $NH_4OH + HCl$.*

Time of reaction, hours	1	5	24	48	96
% NH_4 in the solution	69.0	69.6	69.6	69.3	69.2

When NH_4OH and HCl are added, K-ions are exchanged for NH_4- and H-ions. Since KOH was added four days before NH_4OH and HCl, the K-ions should have had time to become evenly distributed over the surfaces of the resin grain. If this process required a considerable time, the adsorption of the NH_4-ion, too, should do the same. As will be seen from table 11, ionic exchange must have taken place quickly, because the NH_4-concentration in the solution has already become constant after one hour. Thus both experiments have yielded identical results with regard to the velocity of the ion exchange.

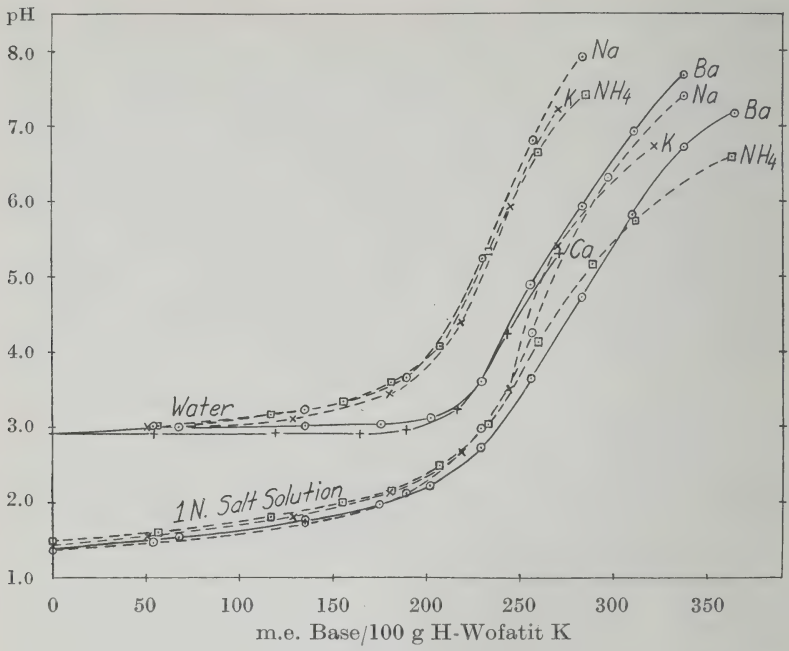


Fig. 22. Neutralization curves of H-Wofatit K in water and in 1 N. chlorides of Na, K, NH_4, Ca and Ba. Broken curves = monovalent ions, continuous curves = bivalent ions.

F. *Neutralization curves.*

Neutralization curves have been made for H-Wofatit K in water and in 1 N. chloride-solutions with Na-, K-, NH_4-, Ca-, and Ba-hydroxydes. 1.000 g of air-dried H-resin was weighed into long pH-tubes and then the calculated amounts of water, salt solution, and hydroxyde were added. The volume of the solution was 50.0 ml. The time of reaction was 48 hours, during which time shaking in a Wagner machine took place several times. After sedimentation pH was determined by means of the glass-electrode in the clear solution. The base binding capacity has been calculated in m.e./100 g of dry H-resin. Figure 22.

As appears from the neutralization curves, the base-binding capacity of the resin up to 180 m.e./100 g is but slightly dependent on the pH of the outside solution. The buffering capacity, $\frac{dB}{dpH}$, is very great in this range. This indicates that the acidoid is strongly protolysed (sulphonic-acid groups). At higher pH-values, to a certain extent, other base-binding groups come into action, which

presumably consist of carboxyl-groups and phenol-groups. At the pH-values prevailing in most of the following experiments, however, these weaker groups were ineffective. In 1 N. salt solution, the curves lie considerably lower and the base-binding capacity is notably higher than is the case in water.

With the aid of the neutralization curves and the amounts of sulphur contained in the resin it was possible to calculate to what an extent the sulphur forms active sulphonic-acid groups. According to the analysis, dry H-Wofatit K contains 7.64 % S corresponding to 238.2 m.e. sulphonic-acid groups per 100 g H-resin. If this value is compared to that which by estimation may be obtained from the titration curves, a rather good agreement will be found. Nevertheless, some sulphur seems to be bound in another way than as ion-exchanging sulphonic acid groups.

3. The Anion Exchange Resin Wofatit M.

Wofatit M is an anion-exchanging resin produced by I. G. Farbenindustrie A.-G. It is a condensation product of aromatic amines with aldehydes, and its functional groups, according to GRIESSBACH (1939), consist of aliphatic amino ($-NH_2$) and imino ($= NH$) groups. Wofatit M, like Wofatit K, has the appearance of black, hard and glassy grains.

The resin was sifted through a 2 mm sieve. Since it was Cl-saturated, the Cl-ions were replaced by OH-ions by leaching with 0.5 N. NH_3. The resin was then washed with distilled water, which was free from carbon dioxide, until the leaching water had become neutral and the reaction for NH_3 had practically disappeared (as verified with Nessler's reagens). It appeared that Wofatit M in an OH-saturated state is not completely stable in distilled water but that a hydrolysis of amino-groups takes place to a minor extent; for this reason, the reaction with regard to NH_3 will not disappear completely when the resin is washed. The OH-saturated resin was dried at first in the vacuum (by means of water suction) and after that by sucking a stream of dry air, free from carbon dioxide, through the material. By this method carbon dioxide was prevented from being adsorbed by the ion exchanger. The resin not being air-dry it was permanently kept in a stoppered container in order to avoid variations of the water contents during the course of the experiments. The contents of dry matter were determined in the same way as for Wofatit K.

A. *Contents of N.*

The OH-resin was analysed only with regard to N, table 7. If the total nitrogen, 18.3 %, would form ion exchanging groups, the acid exchange capacity would amount to not less than 1307

m.e./100 g. However, such a high value seems to be rather improbable; for this reason a great part of the nitrogen must be assumed not to belong to ionogen groups.

B. *Solubility in water.*

If OH-Wofatit M is to be used for anionic exchange, it is of interest to know its stability on leaching with distilled water.

Experiments as to the stability of Wofatit M have been made in the same way as for Wofatit K. 16.00 g OH-resin were weighed into the apparatus mentioned above. The length of the resin column was 14 cm and its diameter 1.3 cm. After some days of soaking the resin was leached with 1000 ml of distilled water, free from carbon dioxide. The water passed through the resin at the rate of 22 ml/minute. The filtrate, which was not alkaline to PP, was acidified with H_2SO_4 and evaporated until 100 ml were left, and then the ammonia was distilled. Calculated per one gram of dry resin and 100 ml of the filtrate, 0.00028 m.e. NH_3 had been dissolved by the leaching.

The dissolution of ammonia has apparently been very low and, with the exception of special cases, must be regarded as being without importance. If the value is compared with the corresponding value of the dissolution of acidic substances from Wofatit K, it appears that Wofatit K is more stable than Wofatit M under the conditions in question.

C. *Neutralization curves.*

In order to investigate both the strength of the basic groups and the acid-binding capacity of the resin, neutralization curves with HCl and H_2SO_4 have been made in water and in 1 N. NaCl and Na_2SO_4. The same methods were applied as for Wofatit K. 1.000 g of OH-Wofatit per 25.0 ml solution. The acid-binding capacity has been calculated per 100 g dry OH-resin. Figure 23.

It appears from figure 23 that Wofatit M is a comparatively weak basoid. The anion-exchange capacity is very high but rather strongly dependent on the pH of the outside solution. In pure water the resin is almost neutral.

The reaction between the resin and the acids can be expressed by the following formulas:

$$R{-}NH_2 + HCl = R{-}\overset{+}{N}H_3 \cdot \overset{-}{Cl}$$

$$R\begin{<}\begin{matrix}NH_2\\NH_2\end{matrix} + H_2SO_4 = R\begin{<}\begin{matrix}\overset{+}{N}H_3\\ \overset{+}{N}H_3\end{matrix} \cdot \overset{--}{SO_4}$$

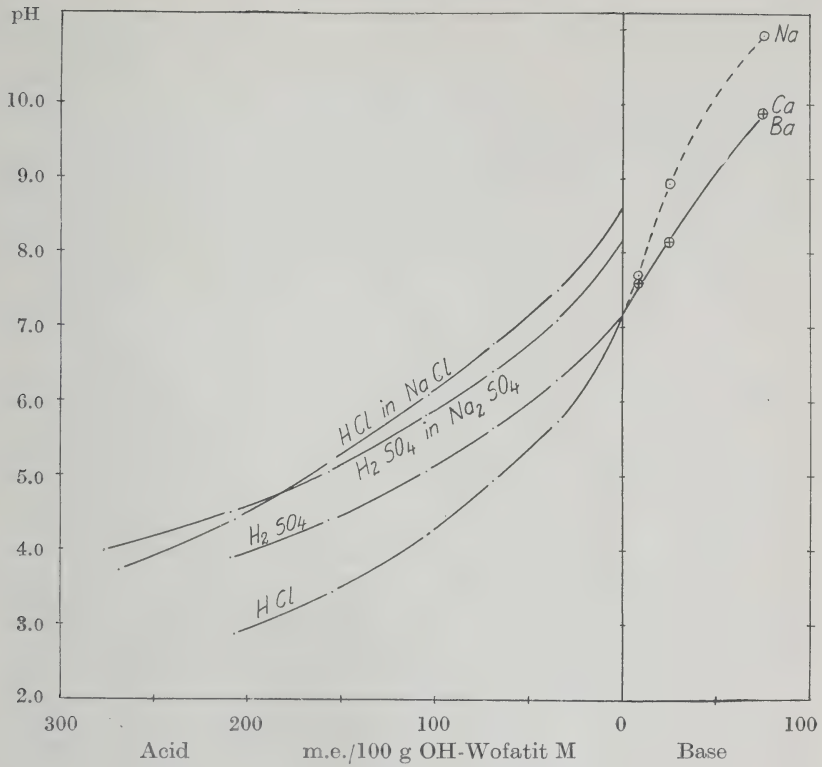


Fig. 23. Neutralization curves of OH-Wofatit M in water and in 1 N. NaCl and Na_2SO_4.

The stronger adsorption of H_2SO_4 as compared with HCl must be primarily ascribed to the fact that the former is bivalent while the latter is monovalent and to the greater decrease of the activity coefficient, caused by this fact, of the SO_4-ion than that of the Cl-ion in the concentrated micellar solution. After all, the conditions are analogous to the fact that, as a rule, a bivalent base is more strongly adsorbed than a monovalent one.

Bhatnagar, Kapur and Puri (1936) and Myers, Eastes and Urquhart (1941) have also noted a greater adsorption of sulphuric acid over hydrochloric acid. These conditions are explained by Myers (1942) by assuming that the sulphuric acid is adsorbed molecularly as a monobasic acid according to the formula:

$$X + H_2SO_4 = X \cdot H_2SO_4 \text{ and not } 2X + H_2SO_4 = X_2 \cdot H_2SO_4$$

In those cases where such an explanation was insufficient, Myers assumes that specific factors, such as hydration and molecular

size of acid, also are operative. However, it is unnecessary to assume such a molecular adsorption, since the stronger adsorption of the sulphuric acid may be explained as a polar reaction in the way mentioned above as will be more fully explained later on.

A partial neutralization is possible and even probable in such cases where the active amino groups are situated so far from each other that both the H-ions in the sulphuric acid molecule cannot be neutralized. Then the reaction must be assumed to take place according to the following formula:

$$R{-}NH_2 + H_2SO_4 = R{-}\overset{+}{N}H_3 \cdot \overset{--}{S}O_4 \cdot \overset{+}{H}$$

Thus, it depends on the structure of the exchanger to what an extent H_2SO_4 is adsorbed as a monobasic or a dibasic acid.

The salt has led to a considerable exchange alkalinity and, by this, to an increase of the acid-binding capacity. While the resin in water has a considerably greater power to bind H_2SO_4 than HCl, conditions in 1 N. salt solution are reversed. Thus the pH-value in chloride-solution without the addition of acid amounts to 8.59, but in sulphate-solution to 8.17, indicating that the Cl-ion at this concentration possesses a considerably higher replacing power than the SO_4-ion. Such conditions may appear embarrassing, if consideration is given to the fact that, at least in the soil colloids, the Cl-ion is slightly adsorbed, but the sulphate strongly. The apparently strange difference between the relative replacing power of the Cl-ion and of the SO_4-ion in water and in 1 N. salt solution is not easily explained; yet a possible cause might be found in an »abnormal» variation of the activity coefficients of the anions in question when the salt concentration is changed. If the neutralization is made in water, the concentration of the Cl- and SO_4-ions in the outside solution is practically zero, and for this reason the activity coefficient in the outside solution may be expected to approach 1. In the inside solution, on the other hand, the activity coefficient of the SO_4-ion is much lower than that of the Cl-ion; this results in a greater replacing power of the SO_4-ion as compared with the Cl-ion. When NaCl and Na_2SO_4 respectively are added, the ionic strength in the outside solution increases and, as a consequence, the activity coefficient of the SO_4-ion decreases much faster than that of the Cl-ion. The activity of the SO_4-ion then becomes very low and as a matter of fact much lower than that of the Cl-ion. When no acid is added, the valence effect is slight, because z in the Donnan equilibrium has a low value and the difference $z+y-x$ is small. Compare part II and Mattson and Larsson (1946). Under such conditions a relatively slightly »abnormal» variation of the activity coefficients for SO_4 and Cl in the inside solution will be

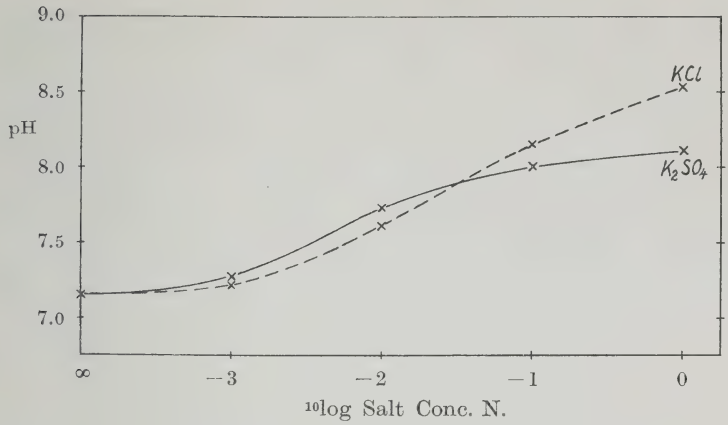


Fig. 24. pH of OH-Wofatit M in 0.001, 0.01, 0.1 and 1 N. KCl and K_2SO_4. 1.00 g resin/25.0 ml solution.

sufficient to overshadow the valence effect and to make the replacing power of the Cl-ion greater than that of the SO_4-ion.

From the results considered above the conclusion may be drawn that in low concentrations sulphates will cause a greater exchange alkalinity than chlorides, but that, with increasing concentration, the difference will decrease, and at high concentration the chlorides will finally become more strongly replacing than sulphates. These conditions have been studied by adding to one gram of OH-resin solutions of KCl and K_2SO_4 in various concentrations and determining pH after 48 hours. The results appearing from figure 24 are in full agreement with the conclusions drawn here.

It will be seen from figure 23 that the neutralization-curves in the NaCl- and Na_2SO_4-solutions more and more approach each other at pH-values below 6, to intersect at pH 4.75. The explanation is presumably to be found:

1) in the valence effect. With decreasing pH the protolysis degree of the resin and the concentration in the micellar solution increase. On account of the fact that the concentration in the outside solution is approximately constant, the difference $z+y-x$ will grow and, in consequence, the replacing power of the SO_4-ion will increase more than that of the Cl-ion;

2) in the fact that at pH-values about 5 the basic properties of the SO_4-ion begin to take effect, which leads to the reaction: $H^+ + SO_4^{=} = HSO_4^-$. On account of the high sulphate concentration and the extremely low H-ion concentration, such a reaction, though being relatively very insignificant, may cause a noticeable increase of the pH-value in the solution.

According to Griessbach (1939), Wofatit M must be regarded as a pure anion exchanger. Still, it may be imagined to contain slightly acidoid groups of a phenol-character which are protolysed only at rather high pH-values. In order to investigate these conditions, neutralization curves in water were made with NaOH, $Ca(OH)_2$ and $Ba(OH)_2$. The results are presented in figure 23.

It appears that Wofatit M at higher pH-values exhibits a rapidly increasing ability of neutralizing bases as is particularly noticeable in connection with Ca- and Ba-hydroxyde. Wofatit M must therefore be characterized as an ampholytoid, the basic as well as acidic groups of which are weak.

V. The Relationship between the Replacing Power ot the H-Ion and the Acidoid Strength and the Position of this Ion in the Lyotropic Series.

1. Introduction.

In part III the replacing power of the more common alkali and alkaline-earth ions on the H-ion has been dealt with. On account of the fundamental importance of the H-ion for many processes and reactions in the soil, it is of interest to study the adsorption intensity of the H-ion. When this is compared with the adsorption intensity of other cations, it will be seen that there is some confusion regarding the mutual order and the factors influencing it. Generally the H-ion is considered to have greater replacement power than most of the other cations, cf. Robinson (1937), Lyon and Buckman (1943) and Millar and Turk (1943). Thus the latter authors give the following order of the replacing power: $Li < Na < NH_4 < K < Rb < Mg < Ca < Ba < Sr < H$. Investigations by Jenny (1927) and Schachtschabel (1940) support the conception mentioned, the former working with permutite, the latter with muskovite, biotite and felspar. A rather weak replacing power of the H-ion in montmorillonitic minerals was, however, found by Jenny (1932) and Schachtschabel (1940).

It is obvious that the replacing power of the H-ion varies considerably according to the nature of the ion exchanging material. The H-ion occupies a unique position, so far as it is often adsorbed very strongly in spite of its low crystallographic ionic radius. It might be expected that the H-ion should be strongly hydrated — as a matter of fact, Pallmann (1938) mentions an ionic diameter in the hydrated state of 10.8 Å, which value, however, must be considered to be too high — and, therefore, to have an activity coeffi-

cient which slowly decreases with increasing ionic strength, and, for this reason, a low replacing power. Compare, for instance, the alkaline ions. The behaviour of the H-ion, which often differs from that of other ions, may yet be interpreted theoretically by applying modern points of view on the problem and, experimentally, by choosing acidoids with widely different strength.

As mentioned in part II, it may be assumed that the acidoids are to be found in two forms, either in a pseudoform with the H-atom bound in a homopolar way or in an aciform in which the H-atom, being bound in a heteropolar way, is protolysable. The two forms are in equilibrium with each other and this equilibrium is ruled by the acidoid strength and the H-ion activity of the outside solution.

$$\text{pseudoform} \rightleftarrows \text{aciform} + H_2O \rightleftarrows \text{acidoid ion} + H_3O^+$$

Only those H-ions which have been set free by protolysation take part in the ionic equilibrium. The weaker the acidoid, the more the equilibrium will be displaced to the left and the lower becomes the H-ion activity in the inside solution. This means that a correspondingly lower H-ion activity in the outside solution is required for the maintenance of the equilibrium; the replacing power of the H-ion increases in the same proportion.

In contrast to the acidoids, the saloids may be considered completely ionized. With the exception of those ions which are associated all the counter-ions directly take part in the equilibrium.

The activity coefficient of the H-ion in the inside solution, calculated for the free H-ions, must be considered rather high. Compare figure 3. Calculated for those H-ions which are replaceable at a certain pH-value, the activity coefficient, on the other hand, becomes highly dependent on the strength of the acidoid and undoubtedly extremely low for weak acidoids. In the outside solution f_H maintains a higher value than most of the other ions. As a consequence of the factors mentioned, *the replacing power of the H-ions becomes a function of:*

1. the ratio between f_H in the outside solution and f_H in the inside solution in relation to the same ratio of other ions present.
2. the strength of the acidoids. With decreasing acidoid strength, the H-ion becomes able to replace other adsorbed ions and compete with them more and more intensely or, in other words, the H-ions become more and more difficult to replace by other ions.
3. the concentration of the micellar solution in relation to that of the outside solution when it is a question of equilibrium between heterovalent ions.

It is evident from what has been said above that, when the replacing power of the H-ion is to be studied in comparison with that

of other cations under conditions when the H-ion is unaffected by the acidoid strength, one must work with an acidoid that is completely protolysed in water. The replacement power of the H-ion will, in this case, not be influenced by the acidoid strength but is only dependent on such factors as are common for other cations. Under these conditions, it ought to be possible to get a conception of the position of the H-ion in the lyotropic series. When the hydration number is taken as a basis, some information about this question may be obtained. It appears from table 2 part II that the hydrated H-ion and the Na-ion must be assumed to have about the same volume and, therefore, may be considered as similar from the point of view of replacement. On the other hand, it is possible to draw certain conclusions by comparing the activity coefficients of the H-ion and of other ions in the same salt solutions. It appears from figure 3 that f_H most nearly agrees with f_{Li} and in such a way that the H-ion will have a somewhat greater replacing power than the Li-ion provided that we have to do with an acidoid that is completely protolysed in water.

Referring to discussions in part II, one should consequently be able to set up, purely theoretically, the following series for the replacement power in an »ideal» acidoid which is completely protolysed in water:

$$Li < H < Na < K < Mg < Ca < Sr < Ba < La$$

For incompletely protolysed acidoids the H-ion ought to move more to the right, the weaker the acidoid.

These conditions have been investigated in four ion-exchangers of very different acidoid strength. To the NH_4-saturated exchangers certain amounts of different chlorides (even HCl) were added, whereafter the amount of NH_4 replaced was determined in the equilibrium solution. The NH_4 replaced can hereby be taken as a measure of the relative replacement power of the cations.

2. Description of the Ion Exchangers Studied.

Arranged after decreasing acidoid strength the following exchangers were used:

A. The resin Wofatit K, the general properties of which have been dealt with in part III.

B. The permutite was of the same kind as used in part III and described there.

C. Vårdsberg clay from the province of Östergötland. With regard to the genesis of the clay, it may be stated that it consists mainly of rock material physically weathered during the glacial period.

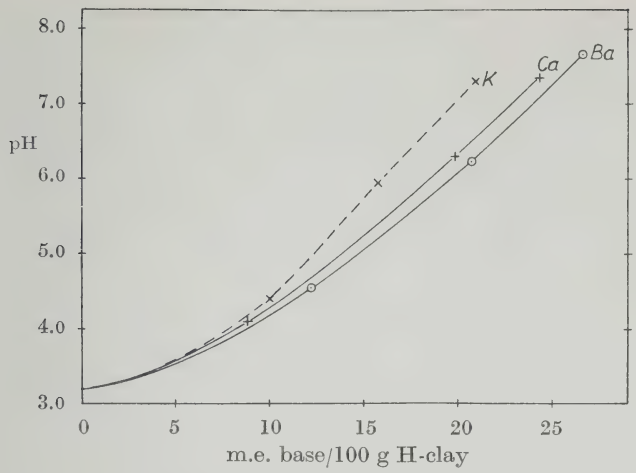


Fig. 25. The neutralization curves of electrodialysed Vårdsberg clay in 0.1 N. KCl, $CaCl_2$, and $BaCl_2$.

The soil was sifted through a 0.2 mm sieve, and then mechanical analysis was carried out. In % of dry matter the composition is as follows: 28.6 % fine sand, 27.5 % silt, 41.4 % clay and 2.0 % organic matter. The soil was electrodialysed in the same way as described above. Neutralization curves were made with the aid of the hydroquinone electrode and by using the methods described in part III. 2.000 g H-soil in 25.0 ml solution. Figure 25.

In spite of the fact that the NH_4-ion was used in the investigation in question, no neutralization curve was made with NH_4Cl because NH_4Cl is noticeably hydrolysed at the neutral point. K- and NH_4-ions agree to a great extent with regard to the ion-exchange properties; for this reason, the K-curve could be used for estimating the ion exchange capacity at pH 7 in 0.1 N. chloride solution.

It appears from the neutralization curves that the cation exchange capacity (C_K, C_{Ca} and C_{Ba}) at pH 7 amounts to 20, 23 and 24 m. e./100 g H-soil respectively.

D. Ordinary bath sponge. The sponge is the cleaned horn skeleton of sea animals belonging to the species Euspongia or Hippospongia. The spongeous skeleton which is left after the decay of the soft parts consists of albuminoids (scleroproteins).

A number of sponges which, regarding quality, were as homogeneous as possible, were chosen and cut into small pieces. These were then treated with dilute hydrochloric acid until all salts had been removed (controlled as to Ca with oxalate) and the sponge was H-saturated. Being freed from chlorides by washing with distilled

water the sponge was dried at room-temperature. The base binding capacity of the H-saturated sponge was determined by successive addition of Na- and Ca-hydroxide, respectively, up to pH 7; the values obtained were $C_{Na} = 51$ and $C_{Ca} = 57$.

Mattson (1942) has worked with electrodialysed sponge and found that it behaves like a weak ampholytoid.

3. Experimental Methods.

Appropriate amounts of the H-saturated ion exchanger were weighed into Erlenmeyer-flasks. A calculated volume of distilled water, which was free from carbon dioxide, was added together with a carefully measured amount of NH_4OH, which was calculated as to be neutralized completely by the acidoid; pH not above 7. Most of the H-ions in the ion exchanger were thus replaced by NH_4-ions. After 24 hours, increasing amounts of the replacing electrolyte were added to the flasks; the amounts were calculated to represent a certain percentage of the number m. e. ammonium ions in the system. A greater amount of ion exchanger was taken at a low concentration of the replacing electrolyte than at a high one, but the ratio between solution volume and the weight of exchanger was ever kept constant, so that the total ammonium ion concentration, too, remained constant. The flasks were shaken every day for a couple of hours during the experimental period. In the flasks containing bath sponge this was squeezed several times with a rubber stopper, attached to a glass rod. After six days' reaction time filtration took place and the ammonia was determined in an aliquot part of the filtrate by distillation; MR + MBl being used as indicator. Both the ammonia solution and the sodium hydroxide used as well as, indirectly, the hydrochloric acid had been adjusted against potassium biiodide as standard titre-solution which was used even in the following experiments.

A longer reaction period has been taken for permutite. Permutite reacts only slowly with bases. Therefore, the ammonium-hydroxide was added successively and in small portions, so that the pH-value never exceeded 7 to any greater extent. Twelve days after the beginning of the saturation the replacing electrolyte was added and, after that, shaking took place for 20 days in the same way as for the other exchangers.

The replaced amounts of NH_4 have been calculated in per cent of the quantities added (and adsorbed by the ion exchanger). However, it has not been possible to correct the values with regard to the volume of the micellar solution ($y_{NH_4} < x_{NH_4}$), for which reason the values must have become somewhat too high. The error is greater at low than at high replacement and will be greater for slightly replacing ions than for strongly replacing ones, the volume of the

micellar solution being greater for the former than for the latter. On account of the fact that the total solution volume has been made great, the calculation error will still be extremely small for the resin and the permutite but a little greater for the clay. For the sponge the micellar water and such water as might be bound in another way, has led to a percentage of replaced NH_4 which is somewhat greater than that which is theoretically possible; this applies particularly to the lower electrolyte concentration. For the mutual comparison of the ions this error has but little importance also in these cases.

4. Experimental Results.

A. *The resin Wofatit K.*

The H-resin was saturated with NH_4 up to 173.8 m. e./100 g dry H-resin. As replacing electrolytes HCl, KCl, $CaCl_2$, and $LaCl_3$ were used which were added in amounts of 30, 60, 100, 150, 200, 400, 800 and 1200 % of m. e. NH_4 in the system. 62.1 ml solution were added per g dry H-resin. The results are shown in figure 26.

The following conclusions can be drawn with the aid of the figure.

1. The replacement power of the ions against the NH_4-ion shows at all concentrations the order: H < K < Ca < La.

2. At low concentrations the rise of the replacement curves shows the following sequence: monovalent < bivalent < trivalent.

This relation is in complete agreement with the Donnan-equili-

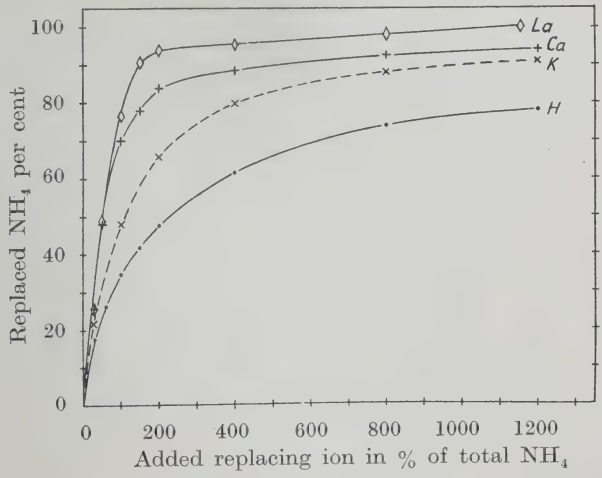


Fig. 26. Replacement of NH_4 from NH_4-resin on addition of HCl, KCl, $CaCl_2$ and $LaCl_3$. The resin saturated with 173.8 m. e./100 g H-resin.

brium, according to which at low concentration bivalent ions will be better adsorbed than monovalent ones and trivalent ions better than bivalent ones.

3. The symmetry value (= % replaced NH_4 at equivalence between replacing ion and total NH_4 in the system) is for H = 34.9, K = 48.4, Ca = 70.2 and La = 76.8.

4. Only La has been able to replace NH_4 completely at the highest concentration. However, a complete replacement is, theoretically, not possible with this method. The cause of the too high value was mentioned above.

In order to study more closely the position of the H-ion in the lyotropic series and in order to confirm the mutual order of the replacing power of the H-ion, the alkali and alkaline-earth ions and the La-ion, which was set up on a purely theoretical basis in the introduction, the following experiments were made. The H-resin was saturated up to 198.6 m. e./100 g dry weight. Judging by the neutralization curves (fig. 22), only the sulphonic-acid groups are then neutralized, for which reason the degree of protolysation of the resin can be considered as generally unchanged. As replacing electrolytes chlorides of H, Li, Na, K, Mg, Ca, Sr, Ba, and La were added in a concentration of 200 % of the total NH_4. The volume of the solution was chosen in such a way that the total NH_4-concentration was the same as in the preceding experiment. The pH in the equilibrium solution was measured with the glass electrode. Duplicates were made in all test-groups. The results are given in table 12.

Table 12. *Replacement of NH_4 from NH_4-resin on addition of chlorides of H, Li, Na, K, Mg, Ca, Sr, Ba, and La. The H-resin saturated with 198.6 m.e. NH_4/100 g dry weight. Conc. of replacing ion = 200 % of m. e. total NH_4.*

Replacing ion	H	Li	Na	K	Mg	Ca	Sr	Ba	La
Air dried resin g	3	3	3	3	3	2	2	2	2
Added NH_4 m. e.	4.80	4.80	4.80	4.80	4.80	3.20	3.20	3.20	3.20
Added solution ml	171.4	171.4	171.4	171.4	171.4	114.3	114.3	114.3	114.3
Replaced NH_4 %	50.7	46.6	57.5	67.8	78.4	84.7	84.9	89.4	94.0
Replaced NH_4 %	51.0	46.4	57.7	67.9	79.1	84.7	85.7	88.6	93.3
pH of equilibr. solution	1.46	2.74	2.71	2.63	2.54	2.45	2.46	2.43	2.30

The following results can be gathered from table 12:

1. The replacement power of the ions lies in the following order:

$$Li < H < Na < K < Mg < Ca < Sr < Ba < La.$$

The order of replacement as advanced above has been satisfactorily confirmed by these experiments. The insignificant difference between the H-ion and the Li-ion is remarkable. It is evident that, when the acidoid is completely protolysed or its degree of protolysation is only slightly changed on addition of a replacing electrolyte, the H-ion will show a replacing power determined by the same factors as are common for other cations.

2. The order within every valence-group and between the groups is in good agreement with the order which was advanced theoretically for an ideal acidoid and which appeared to be valid even for the humus materials. The mutual difference, however, between the more strongly replacing ions cannot become particularly great on account of the high adsorption percentage.

3. The difference between the most strongly replacing monovalent ion, K, and the most weakly replacing bivalent one, Mg, is very great. The explanation of this is probably to be found in the fact that the concentration of the micellar solution is high and consequently also the activity ratio of the inside and outside solutions, which favours the adsorption of the bivalent ions compared to that of the monovalent ones. It has been previously shown that in inorganic exchangers K is usually adsorbed more strongly than Mg.

4. Just as was the case in the H-saturated organic material in part III Sr, here too, has but slightly greater replacement power than Ca.

5. Judging by the pH-value in the solution, besides NH_4-ions, also some H-ions have been replaced by the cation of the salt added. It is interesting to note that even the pH-value in the solution reflects the mutual adsorption tendency of the ions, in so far as the pH-value decreases from Li towards La.

In order to find out to what an extent a higher degree of saturation with NH_4 influences the position of the H-ion in relation to the alkaline ions, an experiment was made in which the resin was saturated with 248.3 m. e./100 g dry H-saturated matter. At such a high degree of saturation one may assume that some H-ions which were not protolysed at lower pH-values might have been replaced by NH_4-ions. In other words, the strength of the acidoid is here likely to begin to influence the adsorption tendency of the H-ion in the way mentioned above. Therefore, it may be said a priori that the replacing power of the H-ion will have increased in comparison with that of the other ions and the H-ion will lie nearer the Na-ion than was the case in the preceding experiment.

Table 13. *Replacement of NH_4 from NH_4-resin on addition of HCl, LiCl, NaCl, and KCl. 248.3 m. e. NH_4/100 g dry H-resin. Conc. of replacing ion = 200 % of NH_4.*

Replacing ion	H	Li	Na	K
Air dried resin g	2	2	2	2
Added NH_4 m. e.	4.00	4.00	4.00	4.00
Added solution ml...	142.9	142.9	142.9	142.9
Replaced NH_4 %	57.0	50.7	61.1	69.5

It appears from table 13 that with higher degree of saturation with NH_4 the adsorption tendency of the H-ion increased more than that of the other ions. The difference between Na and H is smaller but between H and Li it is greater than at the lower degree of saturation with NH_4. This is in complete agreement with the principles postulated.

B. *Permutite.*

The H-permutite was saturated with 73.19 m. e. NH_4/100 g of air-dried H-permutite. The experiment was limited in such a way that only HCl and KCl were used for the replacement of NH_4. Volume of solution = 37.5 ml/g permutite.

From figure 27 may be gathered:

1. The H-ion replaces considerably better than the K-ion. The opposite was the case in the resin. The results are in close agreement with the results obtained by JENNY (1927) with NH_4-permutite.

The difference between the H- and the K-ion has in the experiment probably become somewhat smaller than what it really should have been; this is due to the fact that the acid added has solved some of the permutite.

2. At equivalent concentrations the K- and NH_4-ions have become equally distributed between the permutite and the solution, which means that both ions have the same replacement power on the permutite, provided that the reactions are reversible and that all the ions are accessible.

C. *Vårdsberg clay.*

To the H-soil NH_4OH corresponding to 20.0 m. e./100 g air dried H-soil was added. As replacing ions H, K, Ca, Ba, and La were added in the form of chlorides. The volume of the solution was 10.0 ml/g H-soil. Ba was only used in two concentrations; the points are therefore connected by a straight line.

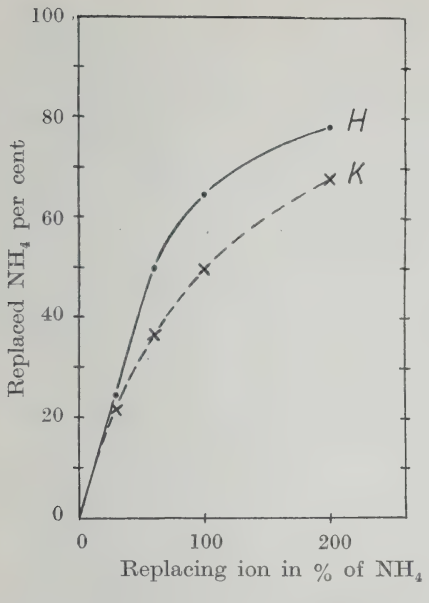


Fig. 27. Replacement of NH_4 from NH_4-permutite on addition of HCl and KCl. 73.2 m. e. NH_4/100 g H-permutite.

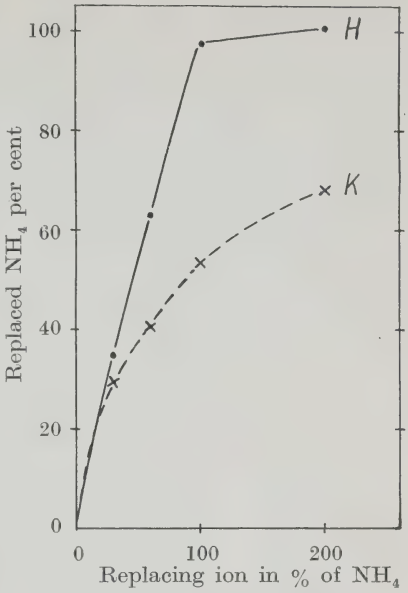


Fig. 29. Replacement of NH_4 from NH_4-sponge on addition of HCl and KCl. 45.0 m. e. NH_4/100 g H-sponge.

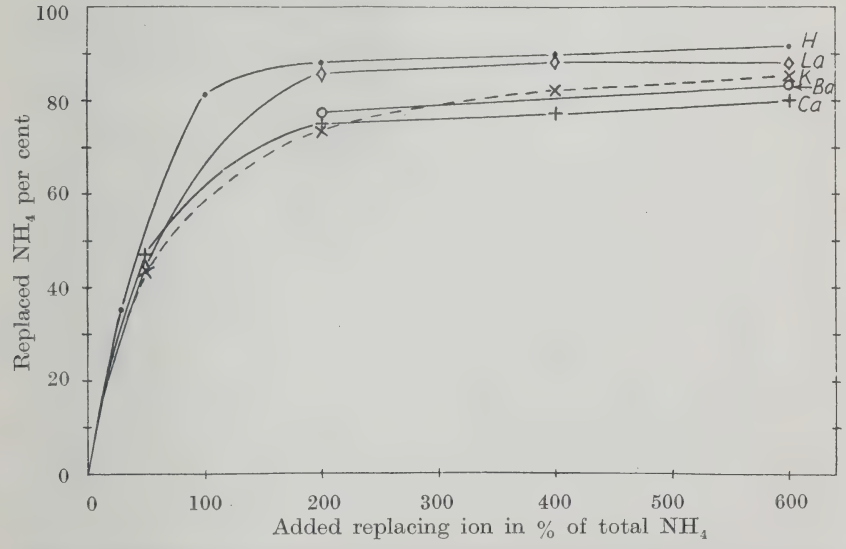


Fig. 28. Replacement of NH_4 from NH_4-Vårdsberg clay on addition of HCl, KCl, $CaCl_2$, $BaCl_2$, and $LaCl_3$. 20.0 m. e. NH_4/100 g H-clay.

The following appears from figure 28:

1. At all concentrations the H-ion replaces best. The curve rises quickly up to 80—90 % of replaced NH_4 and after that slowly. At such a high degree of saturation with H, only the most acidic groups are presumably neutralized; their affinity to the H-ion being low the replacing power of the latter decreases rapidly. Compare the slow rise in the corresponding curve for the resin and the very rapid rise for the bath sponge, figure 29.

2. At low concentrations the K-ion is, in agreement with the theory, adsorbed less intensely than the other ions but at higher concentrations more strongly than Ca and Ba. The replacing power of the ions lies in the order:

below 0.04 N.: $K < Ca < Ba < La < H$
at 0.12 N.: $Ca < Ba < K < La < H$

With regard to the mutual order of the metal cations, Vårdsberg clay behaves on the whole as the H-saturated Ancylus clay in the investigation on the relative pH-reducing power of the cations, cf. table 6. The results from Vårdsberg clay point at a blockade effect or some specific reaction of K in this soil, e.g. by fixation.

D. *Ordinary bath sponge.*

The bath sponge was saturated with 45.0 m. e. NH_4/100 g air dried H-sponge. Replacing electrolytes were HCl and KCl. 60 ml solution on 1 g H-sponge.

From figure 29 the following can be noted:

1. The H-ion is very strongly adsorbed by the bath sponge. Practically, there is equivalence between the HCl added and the NH_4 replaced. The replacement-value at 30 and 60 % HCl-concentration lies somewhat above the value which is theoretically possible; this might be explained by the fact mentioned before that no correction could be made for the water bound by the sponge. The error decreases obviously with increasing concentration as was to be expected.

2. The K-curve has a normal shape. When the degree of the NH_4-replacement on addition of 200 % KCl to resin, permutite and sponge is compared, it appears that the K-ion has replaced practically the same amount NH_4 in spite of the very different character of the ion exchangers. In Vårdsberg clay the K-ion has liberated more NH_4 than in the other exchangers, which is in harmony with the high relative adsorption intensity of K in this soil as established above.

5. Conclusions.

The experiments have shown that the replacing power of the H-ions is intimately dependent on the acidoid strength. Thus, for a completely protolysed acidoid of the type of the sulphonic resin the adsorption tendency of the H-ion is determined by the same factors as determine the adsorption of other cations. For the power of the ions studied to replace NH_4-ions from the resin Wofatit K the following order was found:

$$Li < H < Na < K < Mg < Ca < Sr < Ba < La.$$

Concerning the metal cations this result agrees with the series, set up before for an »ideal» acidoid, which was obtained:

1. by considering the changes of the activity coefficients of the ions with the ionic strength and
2. by applying the Donnan equilibrium to the ionic exchange.

The relative position of H in the series supports the theory of which factors determine the replacing power of the H-ion. *The weaker the acidoid becomes, the more the replacing power of the H-ion increases, and the greater it shifts to the right in the above-mentioned series.* This is due to the fact that a continuously decreasing fraction of the total number of protolysable H-ions takes part in the equilibrium.

If the acidoid contains both strong and weak acidic groups, the replacing power of the H-ion, analogously, becomes a function of the degree of base-saturation in such a way that the adsorption intensity of the H-ion increases more rapidly with the degree of base saturation than that of other ions.

When the H-ion is compared with the K-ion in the four ion-exchangers investigated, it appears that the replacing power of the H-ion increases in the order:

$$\text{Wofatit K} < \text{permutite} < \text{Vårdsberg clay} < \text{bath sponge}.$$

Consequently, the acidoid strength must be assumed to decrease from the left to the right.

It appears from what was said above that, when exchangers of different strength are mixed, or when one ion exchanger has acidoid groups of different strength and irregular distribution, the distribution of the cations adsorbed will vary within the ion exchanging material in accordance with the degree of base-saturation. On a high degree of saturation, high pH, the ions may be approximately evenly distributed but, the more the pH-value decreases, the more irregular becomes the distribution and the less homogeneous the micellar solution. This is, for instance, the case with soil where

the acidoid strength varies with the character of the clay mineral and the humus material.

In analogy with this, SCHACHTSCHABEL (1942) experimentally showed that, when the degree of Ca-saturation at pH 7 was denoted as 100, the corresponding value at pH 5 was for kaolin 91, for montmorillonite 90, for humic acid 75, and for mica 11. Mica is the weakest acidoid and its degree of base saturation declines most rapidly with a decrease in pH. For this reason, mica is able to bind but small amounts of calcium ions at low pH-values.

VI. Amphoteric Reactions of an Aluminium Phosphate Complex.

1. Theoretical Considerations.

In a previous paper by MATTSON and WIKLANDER (1940) the amphoteric reactions of H- and OH-saturated soil colloids have been studied from a purely qualitative point of view, the Donnan equilibrium being used as a basis. Theoretically calculated curves were constructed and these were verified by experimental results obtained by way of determining the exchange acidity and exchange alkalinity on addition of neutral salts. In that paper, however, no analysis was made as to the effect exerted by cations with different replacing power on the shape of the exchange-alkalinity-curve and the position of the maximum point of that curve.

If a neutral salt of the type M_2A is added in increasing concentration to a H- and OH-saturated ampholytoid with equally active basoid and acidoid parts, an ion exchange takes place; the cations of the salt replace H-ions and the anions of the salt replace OH-ions. The pH obtained in the outside solution is determined by:

1. the relative replacing power of the cations and anions,
2. the concentration of the salt,
3. the concentration of the micellar solution, z,
4. the concentration of the colloid, although to a lesser extent (MATTSON and WIKLANDER 1940) and
5. the structure of the colloid in the way dealt with in part III.

From the discussion of the Donnan equilibrium, it appeared that, when the outside solution is diluted, the ratio between the concentration of the bivalent and the monovalent ions within the micelle is changed in favour of the former. If the solution is concentrated the opposite conditions will prevail. This valence effect is most perceptible at low outside concentrations, i. e. at high ratio between inside and outside concentrations. It follows from this that, at high dilution, more anions, A^{2-}, are adsorbed than cations, M^{+}, causing a

greater replacement of OH-ions than of H-ions. With increasing salt concentration, however, the relative adsorption of anions decreases while, at the same time, it increases for cations. The valence effect tends to disappear at high concentrations and the cations and anions to be equally strongly replacing. Therefore, if a sufficient number of small concentration intervals is chosen, a maximum of the exchange alkalinity will be attained.

If K_2SO_4 is added, the reaction takes the following course: When the salt concentration is low, the replacing power of the sulphate ion surpasses that of the potassium ion. More OH- than H-ions migrate out into the solution and the pH-value rises resulting in exchange alkalinity. At very low concentration the exchange alkalinity is small, but with increasing concentration the difference $OH_{replaced} - H_{replaced}$ grows towards a maximum and then decreases. If the active acidoid part is greater than the basoid part, the difference mentioned may become negative resulting in exchange acidity. The position of the maximum and the shape of the curve as a whole are determined by the adsorption-tendency of the K- and the SO_4-ions.

If different alkali sulphates are added, the cations of which have differently strong replacing power while their anions are of the same kind, the course of the curve will not be the same for the various salts. A consideration of the conditions prevailing shows that the maximum point is displaced towards a higher salt concentration, if the replacing power of the cations decreases. Therefore, in case the three salts Li_2SO_4, Na_2SO_4 and K_2SO_4 are chosen, the maximum point will be displaced towards a higher concentration in the order:

$$K < Na < Li.$$

The weaker the adsorption tendency of the cation, the higher the concentration of the salt must be, if the replacement of H is to balance the replacement of OH.

The fact that the activity of sulphate ions in the outside solution increases much more slowly with growing concentration than that of the monovalent ions is an additional reason for the formation of a clearly marked maximum of the exchange alkalinity. According to Hass and Jellinek (1932), f_{SO_4} in 0.01 N. K_2SO_4 solution amounts to only 0.55, while f_K on the other hand amounts to 0.93.

The conclusions drawn above which have been arrived at by theoretical considerations, shall be verified in the following by way of experiments with a synthetic ampholytoid.

2. Experimental Results.

As an amphoteric ion exchanger the electrodialysed aluminium phosphate, $Al_2O_3 \cdot (P_2O_5)_{0.80} \cdot (H_2O)_{4.42}$, described in part III, has

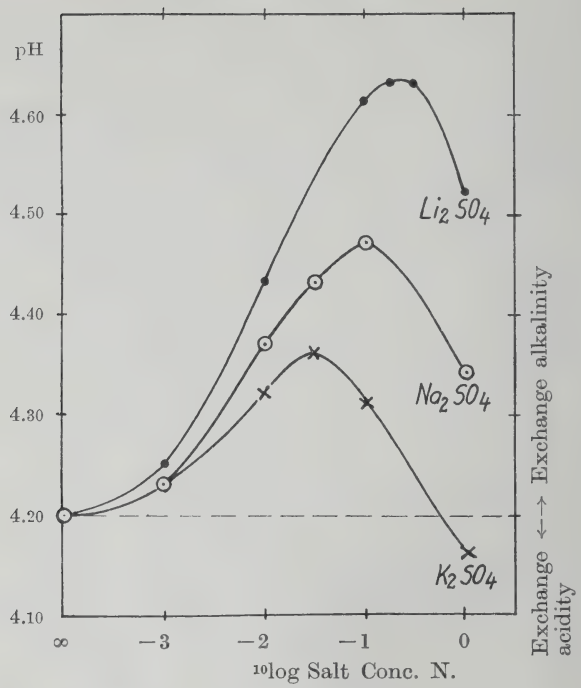


Fig. 30. pH in the suspension of electrodialysed aluminium phosphate on addition of Li_2SO_4, Na_2SO_4 and K_2SO_4. 1.00 g phosphate in 10.0 ml solution.

been used. Owing to its low contents of phosphoric acid it might be expected that its basoid properties would be comparatively strong and that, for this reason, the phosphate would be suitable for amphoteric studies.

1.00 g phosphate was weighed into pH-tubes and 10.0 ml salt solutions of Li_2SO_4, Na_2SO_4 and K_2SO_4 in concentrations ranging from 0.001 to 1.0 N. were added. After shaking as in the case of the concentration-series in part III, pH was determined in the suspension with the aid of the quinhydrone electrode. The results are presented in figure 30.

The following appears from figure 30:

1. The aluminium phosphate gives a considerable exchange alkalinity. Only in the K_2SO_4 solution at the highest concentration the phosphate yields exchange acidity.

2. The exchange alkalinity increases in the order: $K < Na < Li$. This is in accordance with the fact that the H-ion replacing power of these ions decreases in the same order.

3. The maximum point is displaced towards a higher concentration in the sequence: $K < Na < Li$, which is in agreement with the theory. It is evident that the lower the replacing power of the cation, the higher the concentration of the salt must be, if the increase of H-replacement is to surpass the increase of OH-replacement.

VII. The Effect of Dilution on Exchange Equilibria.

1. Introduction.

Fundamentally different opinions as to the effect exerted on the ion exchange equilibrium by dilution with water have been advanced by the research workers, cf. Wiegner (1912), Gans (1913), Kornfeld (1917), Rothmund and Kornfeld (1918), Jenny (1927), Wiegner and Müller (1929), and Weisz (1932), who all have worked with permutite. Some of the authors, above all Rothmund and Kornfeld, asserted that, in comparison with monovalent ions, bivalent ions are adsorbed the better the more the system is diluted. On the contrary, Weisz and others maintained that this conception is erroneous and that the equilibrium is unchanged by addition of water. Also the experimental results obtained by the investigators were not in agreement with each other and no definite conclusions as to the relation existing between the equilibrium and the dilution can therefore be drawn from the data given by the different authors. Compare the historical survey in part II.

As shown before, a discussion of the Donnan equilibrium leads to the conclusion that an intimate interrelation must be presumed to exist between the exchange equilibrium for heterovalent ions and the ratio between the activity in the inside and outside solutions or, in other words, with the dilution of the outside solution. The considerations showed that, on dilution, the adsorption of an ion of high valence is favoured at the expense of an ion of low valence. Also the formulas, advanced by Kerr (1928 a and b), Vanselow (1932), and Gapon (1933) and tested experimentally by Magistad, Fireman, and Mabry (1944), allow similar inferences. But, while these formulas lead to the conclusion that the equilibrium between homovalent ions is not influenced by dilution, it is possible to conclude from the Donnan equilibrium that such a condition is only given if the activity coefficients of the ions taking part in the equilibrium show identical variations when the concentration is changed. For homovalent ions the dilution must consequently be supposed to cause a displacement of the equilibrium in favour of the ion possessing the lower f-value in the inside solution.

These facts are evident if the Donnan equilibrium is written in the following way, taking K and Na as an example:

$$\frac{M_K}{M_{Na}} = \frac{f_{K_o} \cdot f_{Na_i}}{f_{Na_o} \cdot f_{K_i}} \cdot \frac{[K]_o}{[Na]_o},$$

where M_K and M_{Na} signify the adsorbed amounts of K and Na in m. e. and o and i outside and inside solution respectively. If the ratio between the concentrations in the outside solution is constant, it appears from the formula that a dilution will influence the ratio of the adsorbed ions only in case that the f-values vary in a different way. At high dilution the activity coefficients in the outside solution may be put equal and the formula then makes it possible to compute the ratio of the f-values for the adsorbed ions; if the micellar solution is not homogeneous, a mean value is obtained. On dilution the f_i-values vary only slightly.

The equilibrium between a monovalent and a bivalent ion, e. g. K and Ca, may be formulated, if the inside concentration is put equal to $M:v$, by an analogous expression:

$$\frac{M_K}{\sqrt{M_{Ca}}} = \frac{f_{K_o} \cdot f_{Ca_i}^{\frac{1}{2}} \cdot v^{\frac{1}{2}}}{f_{Ca_o}^{\frac{1}{2}} \cdot f_{K_i}} \cdot \frac{[K]_o}{\sqrt{[Ca]_o}},$$

where v expresses volume of the micellar solution which is supposed to be the same for all adsorbed ions. As appears from the formula, the distribution of monovalent and bivalent ions is in addition to concentration and activity coefficients also affected by the volume of the micellar solution. With growing v value, i. e. decreasing micellar concentration, the adsorption tendency of the monovalent ion increases in relation to that of the bivalent ion.

The fact that the adsorption of bivalent ions in montmorillonite is favoured by dilution, is interpreted by SCHACHTSCHABEL (1940) as being a consequence of the more rapid increase of the activity coefficient of the bivalent ion at dilution as compared with that of the monovalent ion. As will be shown in my own experiments, this assumption is not sufficient to explain the strong displacement of the equilibrium which was caused by dilution. The valence effect must be considered as being the dominating factor, cf. the formula above.

The effects of dilution have been studied by MATTSON (1942) in an ordinary bath sponge and by WIKLANDER (1945) in a resin acidoid. MATTSON and LARSSON (1946) examined the valence effect in relation to the micellar ion concentration and the base saturation in kaolin, laterite and bentonite. In contrast to certain of the investigations mentioned above, all these later investigations unanimously proved that the ion exchange equilibrium between heterovalent

ions is influenced by the relation between the concentrations of the inside and outside solutions.

If it is a question of experimentally verifying the inferences deduced from the Donnan equilibrium, it seems to be suitable to use such strong acidoids as, from the point of view of ion exchange, behave as »ideal» exchangers. In such an acidoid the degree of protolysation is independent of the dilution, which is not the case in a weak acidoid; moreover there occur no »abnormities», e. g. ion blockade, or specificities which are common in many other ion exchangers and which may lead to deviations. Therefore, in the experiments carried out here the resin acidoid Wofatit K has been used as cation exchanger. In the aforesaid paper (WIKLANDER 1945) a preliminary report was given of some of the results. Experiments have also been carried out with the resin basoid, Wofatit M.

2. Experimental Results.

Three essentially different methods have been applied for studying the dilution effect.

A. *Alkalimetric determination of the exchange acidity after addition of a neutral salt to the H-saturated resin.*

a. H-resin + chlorides of Li, Na, K, Mg, Ca, and Ba. 3.000 g of air-dried H-resin (= 2.25 g of dry matter) were weighed into Erlenmeyer flasks, whereafter 5.00 m. e. of Li-, Na-, K-, Mg-, Ca- or Ba-chloride, dissolved in distilled CO_2-free water, were added. The volumes of the solutions added amounted to 80, 400 and 2000 ml respectively. The flasks were shaken partly by hand from time to time and partly in the shaking machine. After seven days the resin was allowed to settle, and an aliquot part of the clear solution was titrated, MR + MBl being used as indicator. The exchange acidity thus found was calculated in per cent of the salt added, i. e. of 5 m. e. In the calculations corrections have been made for the volume of the inside solution.

Determination of the volume of the micellar solution. There is no exact method for this determination. By regarding the inside solution as a »saltfree» water film and by determining the negative adsorption of anions SAMUELSON (1944) has been able to compute the volume of the micellar solution, but this method, too, is not indisputable.

An approximate value of the volume of the micellar solution has been obtained by a method which presupposes that a higher underpressure is required during the filtration for removing the inside solution than for removing the outside solution. The outside solution not being bound by the suspended particles it may be sucked away

by but a slight under-pressure. When the whole outside solution has been sucked away, the under-pressure must increase rapidly — a certain pressure-limit is obtained — if the micellar solution is to be separated, because this is tied to the micelle by osmotic forces. If an under-pressure lying somewhat under this limit is applied, the experimentally found volume of the micellar solution is only slightly influenced by minor variations of the under-pressure. The experiments were carried out in the following way.

After titration of the outside solution an appropriate quantity of the resin was transferred to a porcelain filtering-crucible (A2) with ground bottom whereafter the equilibrium solution was sucked away. The filtering flask was attached to a filter pump; the under-pressure was kept constant and amounted to 145 mm Hg which value by repeated trials was found to be suitable. After the solution had been sucked away, the crucible was rapidly weighed. With the experimental method applied practically the same weight was obtained for the crucible containing the moist resin when the measurement was repeated, though the under-pressure and the sucking time varied a little. The weight of the empty crucible in a wet state was determined as the mean of six weighings under the same conditions as for the rest of the determinations. After the determination of the weight of the crucible containing the wet resin, this was quantitatively transferred into weighing bottles and dried, at first at 40–50° C and then in vacuum above P_2O_5 at room temperature. The volume of the micellar solution was calculated in ml/g of dry resin, the density of the water being assumed to be 1. On account of the approximative nature of the method and of the fact that the determinations gave but slight variations in the volume of the micellar solution at different concentrations, a mean value is given for every ion.

As the mean from three determinations, one for each concentration, the following values were obtained:

	Li-,	Na-,	K-,	Mg-,	Ca-,	Ba-resin
micellar solution ml/g dry resin	0.78	0.80	0.70	0.72	0.67	0.62

As is to be expected and was experimentally shown by SAMUELSON (1944), the volume of the micellar solution depends partly on the concentration of the outside solution and partly on the nature of the counter-ion. The comparatively small differences observed in the experiments in question between the volumes of the micellar solution in the different determinations are presumably due to the fact that the counter-ion-swarm consisted of both H-ions and other cations. The quantitative ratio between these has changed and, therefore, the results cannot be compared directly with the values that would have been obtained if the resin had been saturated with only one type of ions.

Table 14. *The effect of dilution on the exchange acidity of H-resin produced by different chlorides. 5.00 m. e. salt and 3.00 g air dried resin.*

Added salt	LiCl			NaCl			KCl		
Solution volume, ml	80	400	2 000	80	400	2 000	80	400	2 000
Replaced H^+ in m. e.	2.41	2.41	2.376	2.814	2.833	2.769	3.17	3.18	3.13
Replaced H^+ in % of m. e. added cation	48.1	48.2	47.5	56.3	56.6	55.4	63.4	63.6	62.6
Added salt	$MgCl_2$			$CaCl_2$			$BaCl_2$		
Solution volume, ml	80	400	2 000	80	400	2 000	80	400	2 000
Replaced H^+ in m. e.	3.88	4.25	4.46	4.08	4.38	4.60	4.27	4.55	4.71
Replaced H^+ in % of m. e. added cation	77.7	85.0	89.3	81.5	87.6	92.1	85.4	90.9	94.2

The exchange capacity and the volume of the micellar solution being known, its concentration can be computed. It follows from the neutralization curves that the exchange capacity of the sulphonic-acid-groups probably lies at about 200 m. e./100 g, which means that the concentration of the micellar solution under the conditions prevailing here amounts to about 2.5—3 N.

The results obtained from the experiment on the effect of dilution are recorded in table 14.

As appears from table 14, the exchange acidity and, with it, the equilibrium between the H-ion and the added monovalent cation have been practically uninfluenced by the 25-fold dilution. When, on the other hand, bivalent cations were added, the exchange acidity increased with the dilution thus indicating that the adsorption of the bivalent cation increased in the same direction. However, no great displacement of the equilibrium may be expected, since the absolute replacement values of the bivalent ions lie comparatively high.

The experiment also reveals the relative H-ion replacing power of the cations in Wofatit K. For a strong acidoid of the type of the resin this capacity could not be determined with the aid of the methods applied in part III, because the pH-value of the H-resin in water already was rather low. At the three salt concentrations applied here, 0.0625, 0.0125 and 0.0025 N., the H-ion replacing power lies in the order:

$$Li < Na < K < Mg < Ca < Ba.$$

The order is the same as that found for the organic materials investigated and which may be considered valid for an ideal acidoid.

Table 15. *Exchange acidity on addition of LiCl, NaCl and KCl to H-resin calculated in m. e./g dry matter.* H_{Li}, H_{Na} *and* H_K *denote the H replaced by Li, Na and K resp.*

Added salt	Conc. of added salt solution N.			
	4	1	0.1	0.01
LiCl	1.75	1.76	1.25	0.40
NaCl	1.83	1.81	1.43	0.46
KCl	1.90	1.88	1.57	0.49
$H_{Na} : H_{Li}$	1.04	1.03	1.14	1.15
$H_K : H_{Li}$	1.08	1.07	1.25	1.23

The marked difference between the monovalent and bivalent ions should be noticed.

b. H-resin + chlorides of Li, Na and K. In the preceding experiment the salt concentrations were throughout low and no displacement of the equilibrium between H, Li, Na and K could be established. Theoretically, however, a displacement of the equilibrium must be expected if the concentration is not too low, since the *f*-value for these ions varies in rather different ways when the concentration changes; compare fig. 3. The above investigations have therefore been supplemented by experiments in which the highest concentration was 4 N. The experiments were carried out in the way described above except that the volume of the added salt solution was 100 ml everywhere. The exchange acidity and the ratio between the hydrogen ions replaced by Na and Li and by K and Li resp. have been computed. The results are recorded in table 15.

As appears from table 15, the exchange acidity grows in the order: $Li < Na < K$. As was to be expected the relative difference decreases with increasing salt concentration. This is most obvious from the calculated ratios. The replacing power of Li in relation to that of Na and K showed some increase from the concentrations 0.01 and 0.1 N. to 1 and 4 N., which is in agreement with the fact that, after having passed a minimum at about 0.15 N., f_{Li} grows rapidly. Most probably the quotient at the highest concentration would have been still lower if not at the concentrations in question f_H grew faster in LiCl than in NaCl and KCl thus counteracting to a certain extent the effect mentioned; compare fig. 3.

B. *Addition of a certain amount of replacing electrolyte to the resin saturated with ions of different valence.*

a. Equilibrium in the system NH_4*-Ca-resin + HCl.* Ca-resin corresponding to 12.00 m. e. Ca together with a calculated amount of

Table 16. *Replacement of NH_4 and Ca on addition of HCl to NH_4-Ca-resin at increasing dilution. In the systems: 12.47 g dry H-resin, 12.00 m. e. NH_4, 12.00 m. e. Ca and 28.59 m. e. HCl.*

Solution volume, ml	80	80	400	2000
NH_4 repl. % of added NH_4	50.0	49.9	52.7	54.9
NH_4 » » » Σ repl. NH_4 + Ca	64.1	64.1	85.4	96.3
Ca repl. % of added Ca	28.0	28.0	8.99	2.11
Ca » » » Σ repl. NH_4 + Ca	35.9	35.9	14.6	3.70
$\frac{\text{Repl. } NH_4}{\text{Repl. Ca}}$	1.79	1.78	5.86	26.0

H-resin were weighed into Erlenmeyer flasks, whereafter distilled water and 12.00 m. e. NH_3 were added. Σ Ca + NH_4 = 192.5 m. e./100 g of dry H-resin. After 1 day 28.59 m. e. HCl were added and so much water that the total volumes of liquid added amounted to 80, 400 and 2000 ml respectively. Consequently, the dilution of the systems, which in other respects were like, was in the ratio of 1 : 5 : 25. After another 7 days' shaking in the way described above, the resin was allowed to settle, whereafter the clear solution was carefully decanted. In the solution Ca was determined by precipitation as oxalate and titration with permanganate, and NH_4 by distillation. The experimental results appear in table 16.

As appears from table 16, the equilibrium between NH_4 and Ca has been strongly displaced with increasing dilution. Thus at the 25-fold dilution the ratio between the replaced amounts of NH_4 and Ca has grown from 1.79 to 26.00. Consequently, when compared with NH_4, Ca becomes more and more difficult to replace by monovalent cations the more the outside solution is diluted; this is in complete agreement with the Donnan equilibrium.

b. Equilibrium in the system Cl-SO_4-resin + NaOH. An appropriate amount of OH-resin was weighed into three Erlenmeyer flasks and CO_2-free distilled water was added. Thereafter the resin was neutralized with 8.00 m. e. HCl and 8.00 m. e. H_2SO_4 . Σ Cl + SO_4 = 167.6 m. e./100 g dry matter. After 1 day 9.6 m. e. NaOH, corresponding to 60 % of Σ Cl + SO_4, were added and the systems diluted with water as in the preceding experiment. Shaking, time of reaction, and decantation were also the same. In the clear equilibrium-solution, the pH of which was about 7, Cl was determined by precipitation with $AgNO_3$ and drying and weighing as AgCl; SO_4 was precipitated as $BaSO_4$, all according to Hillebrand and Lundell (1929).

The experimental results are presented in table 17.

Table 17. *Replacement of Cl and SO_4 on addition of NaOH to Cl-SO_4-resin at increasing dilution. In the systems: 9.54 g dry OH-resin, 8.00 m. e. Cl, 8.00 m. e. SO_4, 9.60 m. e. NaOH.*

Solution volume, ml	80	400	2000
Cl repl. % of added Cl	60.3	74.7	85.0
Cl » » » Σ repl. Cl + SO_4	50.5	61.2	69.2
SO_4 repl. % of added SO_4	59.1	47.5	37.8
SO_4 » » » Σ repl. Cl + SO_4	49.5	38.8	30.8
$\frac{\text{Repl. Cl}}{\text{Repl. } SO_4}$	1.02	1.57	2.25

As appears from table 17, the added OH-ions have replaced about equal amounts of Cl and SO_4 at the lowest dilution but 2.25 times as much Cl as SO_4 at the highest dilution. The equilibrium has thus been displaced in the direction demanded by the theory. In spite of the fact that the displacement of the equilibrium has not been as great as for the corresponding displacement in the NH_4-Ca system, it is still striking enough.

At the lowest dilution, the normality in the outside solution amounts to 0.12 and at the highest dilution to 0.005. According to Hass and Jellinek (1932), the activity coefficients of the Cl- and SO_4-ions in 0.1 M. solution of NaCl and Na_2SO_4 amount to 0.74 and 0.18 respectively and in 0.005 M. to 0.92 and 0.55 respectively. On account of the relatively stronger increase of f_{SO_4} than f_{Cl} on dilution, one might have expected that this, together with the valence effect, would have caused a stronger displacement of the equilibrium than has been the case. At present, it is impossible to ascertain the cause of the low dilution effect. The explanation may yet be found in the fact that, to a certain extent, the sulphuric acid has been adsorbed as a monovalent acid, because some of the active amino groups are sitting too thinly or are too weak to allow a neutralization of both hydrogen ions in the molecule. A certain fraction of the acid then forms monovalent ions (HSO_4^-) in the ion swarm whereby the dilution effect is reduced to a corresponding degree.

It appears from the results of the analyses that the added OH-ions have been used up completely in the replacement of the Cl- and SO_4-ions. This indicates that this resin possesses but weakly basic properties, as is also proved by the neutralization curves in part IV.

C. *Leaching of H-resin with solutions of neutral salts of varying concentration and determination of adsorbed ions after the accomplishment of the equilibrium.*

As neutral salts the systems NH_4Cl—KCl and NH_4Cl—$CaCl_2$ have been used. By adding NH_3 the solutions have been made neutral.

a. System $NH_4Cl + KCl$. The experiment was arranged in the following way. Into five funnels 6 g air dried H-resin were weighed and leached with a neutral solution which was 1 N. with regard to both NH_4Cl and KCl, until about 80 % of the total amount of replaceable H-ions had been replaced. The saturation was then continued by treatment with solutions of NH_4Cl and KCl, in the concentrations 1, 0.1, 0.01, 0.001, and 0.0001 N. with regard to both the NH_4- and the K-ion. The resin was therefore transferred into flasks, a certain volume of solution was added, whereafter shaking took place for a few hours, the solution was decanted, new solution was added, and so on. This procedure was continued until the exchange acidity, tested by methyl orange (MO), had become zero. Leaching took place with a total of 70 liters of the 0.0001 N. solution, every portion consisting of 5 liters. The total time of treatment covered 10 days. The resin was transferred into filtering funnels, the equilibrium solution was sucked away carefully, whereafter the resin was washed free from chloride with CO_2-free distilled water.

NH_4- and K-ions were replaced by hydrochloric acid. The filtrate was analysed as to ammonium by distillation and as to potassium by precipitation with $HClO_4$, drying and weighing as $KClO_4$ according to Wijkström (1935). After the replacement the resin was washed with distilled water and the dry matter was determined by drying in vacuum above phosphorus pentoxide. The results are to be found in table 18 and fig. 31.

b. System $NH_4Cl + CaCl_2$. The system NH_4-Ca-resin was treated principally in the same way as was described for NH_4-K with the exception of the first leaching. Five portions of 4, 4, 5, 6, and 7 g respectively were saturated with solutions of NH_4Cl and $CaCl_2$ which were 1, 0.1, 0.01, 0.001, and 0.0001 N. as to both NH_4 and Ca. A preliminary leaching was carried out in the funnels with NH_4-Ca-chloride-solution, which for funnel 1 was 1 N. as to NH_4 and Ca, while in the remaining funnels the Ca-concentration was increased and the NH_4-concentration was decreased, so that for funnel 5 the composition was 0.4 N. for NH_4 and 1.6 N. for Ca. After about 80 % of the H-ions had been replaced, leaching was carried out with the final solutions mentioned above. By such a procedure, the equilibrium was attained more rapidly in the most dilute solutions.

The fact that the NH_4-Ca-resin is washed with water, the equilibrium solution being sucked away, must be supposed to result in a displacement of the exchange equilibrium in the more concentrated systems. By such a treatment the outside solution is rapidly diluted and the concentration of free salts in the inside solution progressively decreases towards zero. This leads to the result that the adsorption

Table 18. *The adsorption of NH_4-, K-, and Ca-ions by H-resin on leaching with equinormal solutions of NH_4Cl-KCl and NH_4Cl-$CaCl_2$ resp. in the concentrations given below. Adsorbed NH_4 + K and NH_4 + Ca resp. = 100 %.*

Equilibrium solution:					
NH_4Cl Norm.	1.0	0.1	0.01	0.001	0.0001
KCl »	1.0	0.1	0.01	0.001	0.0001
Adsorb. NH_4 + K m. e./g dry H-resin	2.46	2.41	2.36	2.25	2.18
» NH_4 %	43.7	43.9	43.5	43.1	43.7
» K %	56.3	56.1	56.5	56.9	56.3
Adsorb. NH_4 / Adsorb. K	0.78	0.78	0.77	0.76	0.78
NH_4Cl Norm.	1.0	0.1	0.01	0.001	0.0001
$CaCl_2$ »	1.0	0.1	0.01	0.001	0.0001
1. The free chlorides washed away with water.					
Adsorb. NH_4 + Ca m. e./g dry H-resin	2.59	2.69	2.68	2.70	2.62
» NH_4 %	34.9	19.6	7.6	2.7	1.1
» Ca %	65.1	80.4	92.4	97.3	98.9
Adsorb. NH_4 / Adsorb. Ca	0.54	0.24	0.08	0.03	0.01
2. The free chlorides corrected for by analysis.					
Adsorb. NH_4 %	42.0	23.3	8.5	—	—
» Ca %	58.0	76.7	91.5	—	—
Adsorb. NH_4 / Adsorb. Ca	0.72	0.30	0.09	—	—

of Ca increases to a certain extent during the washing and that the adsorption of NH_4 decreases in a corresponding degree. Therefore, the ratio $NH_{4i} : Ca_i$ will be somewhat too low in the 1 N. and 0.1 N. systems and, with that, the valence effect on the dilution too little. In the dilute systems where z in the Donnan equation is relatively large but y is correspondingly low, the displacement will be insignificant.

In order to study the »washing effect» the 1, 0.1 and 0.01 N. systems were repeated in the same way as before but for the washing with water. The equilibrium solution being carefully sucked away in a glass filter funnel, the resin was washed with 800 ml 0.5 N. HNO_3 in small portions. The amount of free chlorides was determined by titrating for Cl according to Mohr in aliquot parts of the filtrate. In correcting for the free salts it was necessary approximatively to put $y_{NH_4} = y_{Ca}$. The error will probably be minute, because some salt from the outside solution was included and in this NH_4 and Ca were present in equivalent amounts. The results from the two procedures are presented in table 18 and in fig. 31.

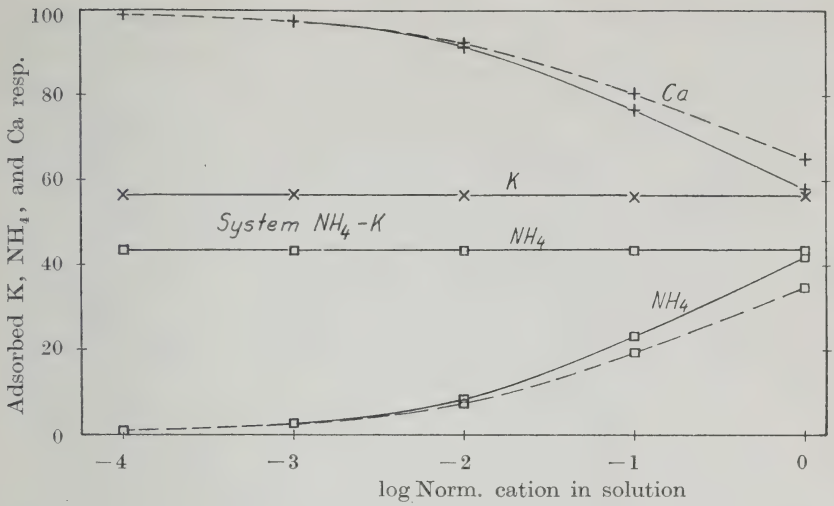


Fig. 31. The adsorption of K, NH_4 and Ca from the systems NH_4Cl-KCl and NH_4Cl-$CaCl_2$ of N. conc. ratios 1:1. Adsorbed NH_4 + K and NH_4 + Ca resp. = 100 %. Dotted curves refer to method 1. Cf. table 18.

As appears from table 18 and figure 31 the relative adsorption of NH_4 and K has not been influenced by the dilution in spite of the fact that the concentration of the outside solution has been decreased 10 000 times. The equilibrium NH_4—Ca, on the other hand, has been strongly displaced in favour of Ca by the dilution; this effect is in agreement with conclusions based on the Donnan equilibrium and the activity concept; cf. the simple calculations in part II:10. Whereas in the 1 N. NH_4Cl—$CaCl_2$ solution the adsorbed ions consisted of 42.0 % NH_4 and 58.0 % Ca, the corresponding values in the 0.0001 N. solution were 1.1 % NH_4 and 98.9 % Ca.

A displacement of the equilibrium of this magnitude cannot be explained exclusively as a consequence of the fact that on dilution the activity coefficient of the Ca-ion in the outside solution grows faster than that of the NH_4-ion, which according to SCHACHTSCHABEL's (1940) opinion was the explanation of the dilution effect in montmorillonite. On the other hand, the valence effect which rapidly grows with increasing dilution can, in connection with the phenomenon just mentioned, be considered as completely responsible for the strong dilution effect observed at equilibrium between NH_4 and Ca.

As it was predicted, the washing with water led to a considerable displacement of the exchange equilibrium. This was especially the case in 1 N., but also in 0.1 N. the change was considerable. In

agreement with the theory the »washing effect» diminished with falling concentration. Thus in 0.01 N. it became insignificant. The results strongly support the conception of the exchange equilibria as ruled by the formula of Donnan.

As appears from table 18 the amount of K- and NH_4-ions adsorbed by the resin decreased considerably with the concentration of the outside solution. The sum of the Ca- and NH_4-ions adsorbed, on the contrary, increased somewhat with the concentration down to 0.001 N. but decreased then. This development is probably due to the fact that the greater adsorption tendency of Ca as compared with that of NH_4 is more effective at low than at high concentration but, as soon as this has gone down to 0.0001 N., this tendency is not sufficient to counteract the effect of the low concentration, since the H-ion begins to interfere, leading to a maximum of adsorbed NH_4 + Ca.

In concentrations smaller than 0.01 N. f_{Na}, f_K and f_{NH_4} can be considered equal. Consequently, these studies make it possible by applying the formula above to calculate the ratios $f_{Na} : f_K$ (from experiments to be published) and $f_{NH_4} : f_K$ in the micellar solution. As average values one gets: $f_{Na} : f_K = 1.96$ and $f_{NH_4} : f_K = 1.30$.

3. Conclusions.

The three different experimental methods applied for studying the effect of dilution have shown conformably

1) that with the ion-combinations and dilutions used, except for the systems Na—Li and K—Li, the equilibrium between monovalent ions is not influenced by dilution;

2) that, on the contrary, the equilibrium between heterovalent ions is influenced in a high degree by dilution. Such is particularly the case for cations, but anions, too, have shown a clear displacement of the equilibrium towards a stronger adsorption of polyvalent ions on increasing dilution;

3) that the results obtained are in good qualitative agreement with the conclusions that can be drawn with the aid of the Donnan equilibrium and of other formulas based on the law of mass action.

In the exchangers used here the ions can be distributed without structural interference; such was not the case in some of the materials used in earlier investigations. That contradictory results have often been obtained with permutite may be explained by structural impediments against the free distribution of the ions.

The alteration of the ion exchange equilibrium of the soil taking place when the soil is dried and wetted and which has been indicated by Mattson and Wiklander (1940), gets additional support

by the present results. The concentration of the soil solution is increased by drying, and by this the bivalent ions (Ca, Mg) in the soil complex are to a certain extent exchanged for monovalent ions (K, Na) in the soil solution. On the other hand, when the soil is wetted, bivalent ions in the soil solutions are exchanged for monovalent ions in the soil complex. The correctness of this conception is corroborated also by the experiments of BURGESS (1922) and HIBBARD (1923). It appears from the results obtained by these investigators that, when wet soil was squeezed, the solution running out contained less K and Na in comparison with Ca and Mg than the extract from the same soil treated with water in the ratio 1 : 5.

Further the valence effect on dilution leads to the conclusion that, if a soil is shaken with distilled water, the composition of the extract will give no true picture of the composition of the soil solution. The contents of Ca and Mg in relation to K and Na will be lower in the extract than in the soil solution.

According to the theory of the uptake of mineral nutrients as worked out by LUNDEGÅRDH (1938, 1940, 1942 and other works) the protoplasm of the root hairs behaves as an amphoteric colloid, which adsorbs and exchanges ions according to the Donnan equilibrium. It may therefore be expected that the effect of dilution should in a certain degree make itself felt also in the uptake of mineral nutrients. Consequently, it is probable that the higher the water contents of the soil, the more easily will the plants take up bivalent ions in comparison with monovalent ions, if the ions are absorbed from the soil solution.

Also from an analytical point of view the valence- and dilution-effects are of interest. If H-saturated resins are used for separating anions and cations, using an apparatus as described briefly in part IV, the time necessary for filtration will, on account of the valence effect, vary according to the valence of the ion to be adsorbed. Usually, experimental solutions are dilute causing polyvalent ions to be adsorbed more rapidly than monovalent ions. The filtering velocity can thus be kept higher for the former than for the latter ones and this in the higher a degree, the more dilute the solution.

VIII. The Influence of Heating on the Exchangeability of the Adsorbed Ions.

1. Introduction.

As pointed out in part III the ion exchange process proceeds rapidly in most of the ion exchangers. However, it has been clearly shown by DAMSGAARD-SØRENSEN (1941) that the accomplishment

of the equilibrium in the case of ionic exchange in permutite may require much time. The equilibrium between NH_4-permutite + NaCl, on the one hand, and between Na-permutite + NH_4Cl, on the other hand, has been studied by DAMSGAARD-SØRENSEN both at 20° C and at 100° C. While no equilibrium had been reached at 20° after a reaction time of 72 days, equilibrium was already reached after 4 hours at 100° C. But also for the ion combinations Na and K an increase in temperature proved to be a means to overcome the inertia of the reaction. When electrodialysed permutites are saturated by neutralization with hydroxides, the process of neutralization is considerably hastened by heating, as was shown by my own investigations.[1] Still, certain risks may be incurred by making use of heating in order to increase the velocity of reaction in ion exchange and in the case of neutralization of H-saturated permutite, if calculations about the ion exchange equilibrium are to be made. A higher temperature may cause exchangeable ions to become more difficult to replace or to become fixed, that is to say pass into a not directly exchangeable form; as a result of this, the calculated states of equilibrium may become faulty, since only exchangeable ions should be considered. Conditions will become still more complicated if the degree of fixation or of the decrease in exchangeability is different for the various ions. If such a reaction takes place, it is also most probable that the tendency of the ions is different with regard to these phenomena. In this direction point, among other things, the individual properties of the ions, the often strong tendency towards fixation to the soil colloids exhibited by K, and the results of PAGE and BAVER (1939).

Permutite and soils being extensively used in the present investigations it has been of interest to make a comparison between the exchangeability of adsorbed cations before and after heating to 100° C. The experiment was arranged in such a way that it was also possible to obtain information as to what an extent the velocity of reaction is dependent on the kind of the ions.

2. Experimental Methods.

The effect of heating on the exchangeability of ions has been studied both in the permutite described in part III and in a clay loam, Vårdsberg clay, of which an account is given in part V as to its mechanical composition and base exchange capacity.

The experiments were carried out with Na, K, Mg, and Ca as adsorbed ions and with HCl as replacing electrolyte.

The electrodialysed permutite was converted into Na-, K- and Ca-permutite by successive addition of small portions of the corres-

[1] Unpublished data.

ponding hydroxides with intervals of several days between the additions. Thus the saturation, which was continued until the outside solution showed neutral reaction and constant pH when kept standing, lasted 75 days. During this time frequent shaking was performed. The permutite was then dried at room temperature and parted into two portions which were transferred into Erlenmeyer flasks. Distilled, CO_2-free water was added. One of the flasks was heated on a steam-bath for 48 hours. The permutite was dried again at room temperature and pulverized. Mg-permutite was produced from H-permutite by repeated shaking and leaching with 2 N. $MgCl_2$. After this treatment the permutite was washed free from chloride with CO_2-free distilled water. Then the Mg-permutite was treated in the same way as the other permutites.

The contents of added cations in the permutites amounted to: for Na 66.8, K 87.3, Mg 45.9, and Ca 80.3 m. e./100 g H-permutite.

Of the different permutites 3.000 g were weighed into Erlenmeyer flasks, distilled water was added, and after two days as much HCl as to correspond to 95 % of the added quantity of cations, measured in m. e. In the Ca-series the volume of water was 300 ml, in the other series the amount of water was chosen in such a way that the total volume of water + HCl-solution was kept constant and equal to 134 ml/1 m. e. added cation. Three different times of reaction were taken, viz. 0.5, 5 and 50 hours of shaking after the addition of the HCl. Immediately after the end of the shaking, filtration took place and the filtrate was analysed as to Na, K, Mg and Ca respectively.

K was precipitated as potassium platinum chloride (Hillebrand and Lundell 1929), Mg as magnesium hydroxyquinolate according to Berg (1935) and Na gravimetrically as Na-Mg-uranyl acetate (Nydahl 1938); Ca was determined as mentioned above. Before the analyses SiO_2 was removed by evaporation with HF and sesquioxydes by precipitation with NH_3 at pH 6.

Apart from the aforesaid series with 95 % HCl, replacement was also performed by adding 400 % HCl with a shaking time of 86 hours.

With regard to the Vårdsberg clay the investigation was limited to K and Ca. A certain amount of the electrodialysed soil was weighed and suspended in water and the soil was converted into K- and Ca-soil respectively by addition of KOH and $Ca(OH)_2$, corresponding to 20.39 m. e. K and 23.00 m. e. Ca per 100 g H-soil or approximately equal to the exchange capacity at pH 7 according to the neutralization curves in fig. 25. One half of the flasks were heated on the steam-bath for 48 hours under occasional shaking, whereafter the suspension was filtered and the soil dried at room temperature and carefully pulverized. From the soils thus treated 8.000 g were weighed into flasks and distilled water and HCl corresponding to 100 % of

the added amounts of K and Ca respectively were added. The total liquid volume was 100 ml. After shaking for 0.5, 5 and 50 hours the amounts of K and Ca replaced were determined in the filtrate.

3. Experimental Results.

The amounts of replaced cations have been calculated in per cent of the quantity of cations added.

A. *Permutite.*

The following appears from the table below:

1. In the permutite in question the ion exchange is apparently a reaction requiring time. This holds true irrespective of the material being heated or not. The velocity of the ion exchange is evidently strongly dependent on the kind of the saturating ion and lies in the order: $Na > K > Ca > Mg$.

Table 19. *Replacement of Na, K, Mg, and Ca on addition of HCl to permutite which was either unheated or preheated to 100° C for 48 hours at varying time of reaction.*

Time of reaction	Added HCl %	Replaced ions in % of total		Difference unheated–preheated	pH of filtrate	
		Unheated	Preheated at 100°		Unheated	Preheated
		Na-permutite.				
0.5	95	72.7	70.6	2.1	3.83	3.45
5	»	80.5	76.4	4.1	4.06	3.77
50	»	85.2	80.1	5.1	4.30	3.98
86	400	97.3	95.7	1.6	3.33	3.09
		K-permutite.				
0.5	95	53.7	46.0	7.7	3.33	3.01
5	»	58.1	49.6	8.5	3.71	3.34
50	»	65.3	52.9	12.4	3.93	3.65
86	400	81.8	77.1	4.7	3.14	2.87
		Mg-permutite.				
0.5	95	41.7	34.5	7.2	3.29	3.15
5	»	50.0	43.2	(6.8)	3.78	3.46
50	»	65.7	52.1	13.6	3.90	3.73
86	400	74.5	67.4	7.1	3.34	3.18
		Ca-permutite.				
0.5	95	50.6	43.3	7.3	3.40	3.00
5	»	58.4	50.8	7.6	3.80	3.39
50	»	68.9	60.0	8.9	3.92	3.66
86	400	86.5	82.0	4.5	3.18	2.92

2. The heating of the permutite in water to 100° C has led to a decrease in the exchangeability of the saturating ion. This appears directly from the values obtained and indirectly from the pH-values in the filtrates. Throughout, the pH is higher in the samples which had not been heated, indicating that more H-ions have entered. No rigid equivalence between the H-ions exchanged and the cations replaced can be expected, since at the pH-values prevailing here part of the permutite is dissolved and, for this, H-ions are used.

3. The difference between unheated and preheated permutite increases with the length of the time of reaction, when constant amounts of acid are added. At the beginning of the reaction the ions which are most easily exchangeable are replaced, but the more the exchange of the ions progresses, the more difficult the exchange becomes and the more marked the difference between the two permutites. Compare the fifth column of the table.

4. As predicted, the exchangeability of the various ions has been affected in a different degree by the heating. The decrease of the exchangeability lies in the following order:

$$Na < Ca < K < Mg.$$

Na in particular has been scarcely influenced. It is interesting to note that Mg and K, both of which exist in soil colloids chiefly in the nonexchangeable form, here behaved in the same way and that the exchangeability decreased considerably.

5. By addition of increased amounts of acid and longer time of shaking the difference between the two permutites has been considerably reduced but, still, it is great for the K-, Ca- and particularly the Mg-saturated permutites.

Heating has led to a certain »fixation» of the ions but, at increased H-ion concentration, this could be partly overcome. The stronger replacement on increased addition of acid must partly be ascribed to the fact that a greater part of the permutite has been dissolved at the higher than at the lower HCl concentration.

B. *Vårdsberg clay.*

Table 20. *Replacement of K and Ca on addition of HCl to Vårdsberg clay, which had either not been heated or preheated to 100° C for 48 hours; 50 hours' shaking time. Added HCl equivalent to K and Ca respectively.*

	Replaced ions in % of total		Difference unheated–preheated	pH of filtrate	
	Unheated	Preheated		Unheated	Preheated
K-clay	75.2	69.4	5.8	3.18	2.71
Ca-clay	80.0	77.1	2.9	3.20	2.80

As appears from table 20, the heating of the Vårdsberg clay has led to the effect that the adsorbed ions have become more difficult to replace, and, as in permutite, this effect is more marked for K than for Ca. These conditions are also reflected in the pH-values of the filtrates.

4. Discussion.

The experiments with permutite and the clay have shown that heating in water to 100° C causes the exchangeability of the adsorbed ions to decrease. The decrease is of different magnitude for the various ions and proved to be considerably greater for K and Mg than for Na and Ca. To the same extent as the ions become fixed by the heating they are kept beyond the direct ion exchange equilibrium. As shown by Bray and DeTurk (1938), DeTurk, Wood and Bray (1943) and others, there is an equilibrium between fixed and not fixed K. The same conditions might be imagined to exist for other fixed ions. But since fixed ions are very slowly, if at all, replaceable, they do not directly take part in the exchange equilibrium. The application of heat to permutoid ion exchangers, in order to hasten the accomplishment of the equilibrium and in the case of the neutralization, may therefore lead to the consequence that the calculations of the equilibrium become more or less faulty.

With regard to the effect caused by heating of an ion exchanger, it may be expected that the counter-ions, apart from an increased thermic motion, are completely or partly dehydrated, that the lattice or the structure of the ion exchanger becomes more open, and that possible specific reactions, as lattice ion exchange etc., are accelerated.

The results obtained by Jaeger (1929) when studying ionic exchange on ultramarine indicate that ions are dehydrated at higher temperatures. Ag-saturated ultramarine was treated in sealed glass tubes with alkali halogenides at 100°, 130° and 160° C, whereby both the time of reaction and the concentration were varied. It appeared that at 130° and 160° the replacing power of the alkali ions had the order:

$$Li > Na > K > Rb > Cs.$$

The velocity of the ionic exchange also decreased in the same direction. This order is in agreement with that which was to be expected a priori, if the ions were not hydrated, but reversed as compared with the order of the hydrated ions.

The decreased exchangeability caused by preheating in the present experiment may partly be ascribed to real fixation, partly to the fact that the ions, on account of the decrease of their apparent effective volume, more easily get access to inner surfaces or parts

of the ion exchanger which otherwise are difficultly accessible. The possibility of a »lattice»-ion-exchange must also be assumed to be considerably greater at higher than at lower temperature on account of the increased thermic motion of the ions to be found in the lattice or in the amorphous substance.

Presumably, the decrease in the exchangeability of the ion by heating is not limited to permutite and to the clay investigated, but may be assumed to take place in other inorganic ion exchangers too. This is indicated by the results obtained by PAGE and BAVER (1939) on montmorillonitic clays. PAGE and BAVER studied the fixation of alkali and alkaline-earth ions caused by drying at 100° C, the results are therefore not directly comparable. Still, it is of interest to note that the ions showed considerable variations in the degree of fixation and that K, as in my experiments, was fixed strongly. Mg on the other hand showed a comparatively low fixation, considerably lower than K, but somewhat stronger than Ca.

IX. The Influence of the Degree of Saturation of the Exchanger and of the Nature of the Complementary Ions on the Exchangeability of Adsorbed Ions.

1. Introduction.

Among soil scientists and agricultural chemists the most predominant conception is that the exchangeability of an ion decreases successively with its relative part in the exchangeable ions. This would mean that an ion is the more strongly bound and that its replacing power is the greater, the lower the degree of saturation of an exchanger for the ion in question. The saturation degree, D_M, of an exchanger with respect to an ion, M, may be expressed by the formula;

$$D_M = \frac{M \cdot 100}{M + C},$$

where M denotes the amount of the ion in m. e. and C the sum of m. e. of other adsorbed ions, generally called *complementary ions*.[1] If the exchanger is saturated with one kind of ions only, the ions should, according to the dominant conception, be most easily replaced, but if other ions are present, the exchangeability should decrease with falling degree of saturation, and this

[1] To denote certain ions as complementary ions is of course arbitrary. Any ions may be considered as complementary; decisive in that respect is what ion is to be studied.

would be the case *irrespective of the nature of the complementary ions.* Therefore, it should involve great difficulties completely to replace an ion. From an agricultural point of view, regarding particularly the absorption of nutrients by the plants, the availability of the minor elements, the retention of nutrients in the soil, and regarding further the use of ion exchanging substances in analytical chemistry etc., this problem is of very great interest. Earlier investigations in this sphere are generally exclusively concerned with the relation between the saturation degree of soil colloids with respect to an ion and its availability to plants (Horner 1936, Yarussov 1938, Mehlich and Colwell 1943 and 1946, Marshall 1944 b, Allaway 1945).

The opinion mentioned is held, among others, by Weisz (1932) and Yarussov (1937), and by Schachtschabel (1940) who studied ion exchange in a number of clay minerals. Schachtschabel writes: »Dies bestätigt die Annahme, dass die Ionen um so fester gebunden werden, je geringer ihr Anteil am Ionenbelag ist.» However, Schachtschabel has not made any detailed analysis of the problem, and he does not mention anything about a possible influence of the complementary ion on the exchangeability of an ion. The opinion mentioned is held also by Jenny and Ayers (1939), who studied the relation between the degree of saturation with respect to an ion and its exchangeability and absorption by plant roots and, in connection with that, the influence of the complementary ion. They write: »The present study convincingly shows, both by experiment and by theory, that the replaceability of a cation from a clay particle is depressed by the presence of complementary ions.» Notwithstanding the fact that the results gained by Jenny and Ayers are of great interest and in good agreement with the theoretically constructed exchangeability curves, it must be emphasized that the authors have drawn too far-reaching conclusions. The cause of this is to be found in their experimental method as well as in the presumptions made for the calculated curves. Allowing the degree of saturation with a certain ion to fall from 100 % towards 0, Jenny and Ayers simultaneously diminished the concentration of the replacing ion and, moreover, in such a way that the total concentration of this ion and that of the ion studied were always equal. With absolute necessity such an experimental method must result in a less and less percentage replacement of the ion studied, since progressively increased relative quantities of the complementary ion are being released. Consequently, such an experimental method cannot answer the question whether a diminishing degree of saturation also implies decreasing exchangeability or not.

An essentially differing conception is held by Bray (1942), who asserts that the exchangeability of an ion is not determined by the degree of saturation but by its own ability of release and by the

nature of the complementary ions. From replacement experiments with natural soils and HCl BRAY obtained constants which he considered as a measure of the relative exchangeability of the ions at low replacement on similar soils. It appears, however, from BRAY's analytical results that the soils examined behaved in rather different ways. Thus the exchange capacity varied between 9.9 and 37.9 m. e./100 g soil, which should have influenced the constants for the ability of release.

Only if soils are very like each other with regard to such properties as are connected with ion exchange, it is possible to use the same constants. Knowing the valence effect on dilution it is possible to state that the relative exchangeability of heterovalent ions should vary with the concentration of the micellar solution; this, in its turn, is dependent on the base exchange capacity, the degree of base saturation, and the acidoid strength. If, for example, the colloids have highly different contents of exchangeable bases (different concentration of the micellar solution), the exchangeability of ions of different valence will vary more or less from one exchanger to the other on addition of an equal amount of replacing electrolyte and, in consequence, the percentage of the replaced amount of each ion. This is also the case if there is only a small amount replaced. Therefore, it is not possible to propose a direct proportionality between the replaced amount of any ion and the fraction of this ion and all the replaceable ions irrespective of the valency.

Still, judging from his discussions and experiments, BRAY has evidently not considered these circumstances. The great variation of the »exchange constants» found in BRAY's experiment may probably be considered as due partly to the circumstances mentioned above, partly to a varying degree of saturation with different ions, and partly to the nature of the complementary ions.

2. Theoretical.

Taking the activity concept and the law of mass action as a basis I will try to elucidate *the relationship* existing between *the exchangeability* of an ion, *the degree of saturation* of the colloid with this ion, and *the nature of the complementary ions*. In the following discussion an acidoid saturated with Na-, K-, H-, Mg-, Ca-, and La-ions is presupposed. All these cations are ionized and their activity in the micellar solution — associated ions also included — is denoted by $(Na)_i$, $(K)_i$, $(H)_i$, $(Mg)_i$, $(Ca)_i$ and $(La)_i$ respectively. Further no ion blockade is supposed to exist with regard to the replacing ion. As a replacing electrolyte HCl is used. The exchanger containing the micellar water is assumed to be added to the HCl solution, the hydrogen activity of which is denoted as $(H)_o$. *At*

low percentage replacement the quantity of adsorbed ions replaced will be proportional to the activity of each ion (measured in normality) in the micellar solution and to the activity of the hydrogen ions in the outside solution; both of them being measured before the beginning of the reaction. The activity coefficient of the ions in the micellar solution and that of the hydrogen ion in the outside solution are considered unchanged or but slightly influenced by the exchange. This presumption will hold true, if the addition of HCl is small as compared with the total amount of the replaceable ions and if, consequently, the percentage exchange is small. Under these presuppositions the quantities of released ions may be expressed thus:

$$R_{\mathrm{Na}} = k_1 \cdot (\mathrm{Na})_i \cdot (\mathrm{H})_o \tag{10}$$

$$R_{\mathrm{K}} = k_2 \cdot (\mathrm{K})_i \cdot (\mathrm{H})_o \tag{11}$$

$$R_{\mathrm{H}} = k_3 \cdot (\mathrm{H})_i \cdot (\mathrm{H})_o \tag{12}$$

$$R_{\mathrm{Mg}} = k_4 \cdot \sqrt{(\mathrm{Mg})_i} \cdot (\mathrm{H})_o \tag{13}$$

$$R_{\mathrm{Ca}} = k_5 \cdot \sqrt{(\mathrm{Ca})_i} \cdot (\mathrm{H})_o \tag{14}$$

$$R_{\mathrm{La}} = k_6 \cdot \sqrt[3]{(\mathrm{La})_i} \cdot (\mathrm{H})_o \tag{15}$$

R_{Na}, R_{K}, R_{H}, R_{Mg}, R_{Ca}, and R_{La} denote replaced amounts in m.e. of Na, K, H, Mg, Ca, and La respectively. It is then possible to get the following expression, where R_T means the total amount of replaced ions:

$$R_{\mathrm{Na}} + R_{\mathrm{K}} + R_{\mathrm{H}} + R_{\mathrm{Mg}} + R_{\mathrm{Ca}} + R_{\mathrm{La}} = R_T,$$

and since it must also be true that $k_1 = k_2 = k_3$ and $k_4 = k_5$ (because k is only a proportionality factor and $(\mathrm{H})_o$ is the same in all exchange reactions), we obtain the expression:

$$R_T = (\mathrm{H})_o \cdot \left[k_1 \cdot [(\mathrm{Na})_i + (\mathrm{K})_i + (\mathrm{H})_i] + k_4 \cdot \sqrt{(\mathrm{Mg})_i} + k_4 \cdot \sqrt{(\mathrm{Ca})_i} + k_6 \cdot \sqrt[3]{(\mathrm{La})_i}\right] \tag{16}$$

The quantity of replaced Na is derived from the equations (10) and (16), k_1 and k_2 being new constants:

$$R_{\mathrm{Na}} = \frac{(\mathrm{Na})_i \cdot R_T}{(\mathrm{Na})_i + (\mathrm{K})_i + (\mathrm{H})_i + k_1 \cdot \sqrt{(\mathrm{Mg})_i} + k_1 \cdot \sqrt{(\mathrm{Ca})_i} + k_2 \cdot \sqrt[3]{(\mathrm{La})_i}} \tag{17}$$

If concentration is substituted for activity, the quantity of replaced sodium is determined by the following expression:

$$R_{Na} = \frac{f_{Na} \cdot [Na] \cdot R_T}{f_{Na} \cdot [Na] + f_K \cdot [K] + f_H \cdot [H] + k_1 \sqrt{f_{Mg} \cdot [Mg]} + k_1 \sqrt{f_{Ca} \cdot [Ca]} + k_2 \sqrt[3]{f_{La} \cdot [La]}}, \quad (18)$$

where [ ] denotes the concentrations in the micellar solution before the beginning of the reaction.

Taking sodium as an example one gets the relation $[Na] = \frac{M_{Na}}{v}$, where v means the volume of the micellar solution and M_{Na} m. e. exchangeable Na; M_{Na} and v refer to the same quantity of the ion exchanger. Making the approximation that all exchangeable ions are distributed in the same micellar solution volume, v, it is consequently possible to exchange concentration in formula (18) for the total amount of exchangeable ions, signified by M_{Na}, M_K, M_H, M_{Mg}, M_{Ca}, and M_{La} m. e. respectively, the total amount of which is equal to the exchange capacity C. Then, formula (18) assumes the form:

$$R_{Na} = \frac{f_{Na} \cdot M_{Na} \cdot R_T}{f_{Na} \cdot M_{Na} + f_K \cdot M_K + f_H \cdot M_H + k_1 \sqrt{f_{Mg} \cdot v \cdot M_{Mg}} + k_1 \sqrt{f_{Ca} \cdot v \cdot M_{Ca}} + k_2 \sqrt[3]{f_{La} \cdot v^2 \cdot M_{La}}} \quad (19)$$

Formula (19) is suitable for computing the replacement of *homovalent* ions at any degree of saturation. For this use the formula can appropriately be written in a more general form:

$$R_A = \frac{f_A \cdot M_A \cdot R_T}{f_A \cdot M_A + f_B \cdot M_B + f_C \cdot M_C + \cdots + f_x \cdot M_x} \quad (20)$$

The ions A, B, C etc. have the same valence but may be mono- or polyvalent.

If one computes the replacement of monovalent ions in the presence of polyvalent ones, it will be found that formula (19) yields somewhat too low values as is indicated by a slightly marked minimum in that part of the replacement curve where the degree of saturation for the monovalent ions approaches 100 % (Cf. fig. 34). Still, it is possible to modify the formula in such a way that this tendency will disappear. If the adsorbed ions are homovalent, v will cancel out of the formula, which is not the case if the ions are heterovalent. If an exchanger saturated with Na and Ca only is taken as an example, v should have its relatively greatest importance in case the adsorbed ions exclusively consist in Ca, provided that the replacement is carried out with monovalent ions, and should decrease successively according as the degree of saturation

with Ca ($= D_{Ca}$) falls and D_{Na} grows. This relationship can be expressed by multiplying v by the fraction $\frac{M_{Ca}}{M_{Na} + M_{Ca}}$. Consequently, a more correct formula, valid at any degree of saturation, for computing the replacement of Na with Ca as complementary ion will read as follows:

$$R_{Na} = \frac{f_{Na} \cdot M_{Na} \cdot R_T}{f_{Na} \cdot M_{Na} + k \cdot \sqrt{f_{Ca} \cdot \frac{M_{Ca}}{M_{Na} + M_{Ca}} \cdot v \cdot M_{Ca}}} \qquad (21)$$

Moreover, the formula indirectly makes possible the calculation of R_{Ca} by subtracting R_{Na} from R_T.

Formula (19) is not applicable for directly computing the release of bivalent ions in the presence of monovalent ones. Still, it is possible to deduce a formula useable for the replacement of bivalent ions at all degrees of saturation. The replacement of bivalent ions is then supposed to be proportional to $(H)^2$ in the outside solution, before the beginning of the reaction, which is in agreement with the ion exchange formula:

$$\overset{++}{Ca}_i + 2\overset{+}{H}_o \rightarrow 2\overset{+}{H}_i + \overset{++}{Ca}_o,$$

resulting in:

$$R_{Ca} = k_1 \cdot (Ca)_i \cdot (H)_o^2 \cdot$$

If the Na-, K-, H-, Mg-, and Ca-ions are included, the following expression is obtained:

$$R_{Ca} = \frac{R_{Ca}}{R_{Ca} + R_{Mg} + R_{Na} + R_K + R_H} \cdot R_T.$$

If in the fraction of this formula the preceding expression is substituted for R_{Ca} as well as the corresponding expressions for the other ions, the result becomes:

$$R_{Ca} = \frac{k_1 \cdot (Ca)_i \cdot (H)_o^2 \cdot R_T}{k_1 \cdot (Ca)_i \cdot (H)_o^2 + k_2 \cdot (Mg)_i \cdot (H)_o^2 + k_3 \cdot (Na)_i \cdot (H)_o + k_4 \cdot (K)_i \cdot (H)_o + k_5 \cdot (H)_i \cdot (H)_o}, \qquad (22)$$

where the constant $k_1 = k_2$ and $k_3 = k_4 = k_5$. If the numerator and the denominator are divided by $(H)_o^2$ and k_1, and if then $(H)_o$ is exchanged for $\frac{R_{Na}}{k_3 \cdot (Na)_i}$, $\frac{R_K}{k_4 \cdot (K)_i}$ and $\frac{R_H}{k_5 \cdot (H)_i}$, and if the total amounts of adsorbed ions are inserted in the way mentioned above, the equation changes thus:

$$R_{Ca} = \frac{f_{Ca} \cdot M_{Ca} \cdot R_T}{f_{Ca} \cdot M_{Ca} + f_{Mg} \cdot M_{Mg} + \frac{k}{v} \cdot f^2_{Na} \cdot \frac{M^2_{Na}}{R_{Na}} + \frac{k}{v} \cdot f^2_{K} \cdot \frac{M^2_{K}}{R_K} + \frac{k}{v} \cdot f^2_{H} \cdot \frac{M^2_{H}}{R_H}} \quad (23)$$

This formula has, however, one disadvantage: the occurrence of R_{Na}, R_K and R_H. Yet, it is possible to calculate those quantities from formula (19). In case the exchanger contains one bivalent ion and one monovalent ion only, it is convenient to combine (21) and (23), which removes the disadvantage. If thus the two ions are Ca and Na, a combination of (21) and (23) makes it possible directly to compute the replaced amount of Ca from the formula:

$$R_{Ca} = \frac{f_{Ca} \cdot M_{Ca} \cdot R_T}{f_{Ca} \cdot M_{Ca} + \frac{k_1}{R_T \cdot v} \cdot \left(f^2_{Na} \cdot M^2_{Na} + k_2 \cdot f_{Na} \cdot M_{Na} \cdot M_{Ca} \cdot \sqrt{\frac{f_{Ca} \cdot v}{M_{Na} + M_{Ca}}} \right)} \quad (24)$$

The following conclusions may be drawn from the deduced formulas concerning the factors determining the release of adsorbed ions.

1. If all the ions have the same valence, the amount of an ion that is replaced on addition of a small quantity of an electrolyte will be determined by the activity coefficients and the relative amounts (saturation degrees) of all the ions as well as by the total amount replaced. The volume of the micellar solution, however, has no influence, as v cancels out of the formula, whereas in case of different valence of the ions also the volume of the micellar solution will be of importance for the quantity replaced, the influence of the volume being greater, the higher the valence of the complementary ions.

2. The higher the activity coefficient of a certain ion in relation to that of the complementary ions, the greater will be its percentage replacement.[1]

3. The percentage replacement of an ion increases with falling activity coefficient of the complementary ion and vice versa.

4. The greater the difference between the activity coefficient of a certain ion and that of the complementary ions, the more the exchangeability of the ions will be influenced by a varying degree of saturation.

5. The degree of saturation being constant an ion will be more difficult to replace, if a complementary ion with a low activity coefficient is exchanged for another ion with a high coefficient. On the other hand, the exchangeability increases if an ion with

[1] Computed according to $\frac{R_{Na} \cdot 100}{M_{Na}}$

a low activity coefficient is substituted for a complementary ion with a high one. This is in agreement with BRAY's (1942) conclusion.

6. Further the following very important conclusion as to the effect of the saturation degree on the exchangeability of the homovalent ions may be drawn from formula (20). If the ions present have different activity coefficients, the exchangeability of any of those ions must vary with a change of the saturation degree of any of the ions in question. Consequently, the exchangeability of an ion changes, even if the saturation degree is constant for this ion but changed for the complementary ions. In case the ion exchanger is saturated with two kinds of ions, the exchangeability of the ion with the higher coefficient will grow with a falling degree of saturation, whereas, in the same case, the exchangeability of the ion with the lower coefficient will diminish.

An exchanger saturated with Na and K only may be taken as an example of these conditions. At the high ionic strength prevailing in the micellar solution, Na has a considerably higher activity coefficient than K irrespective of the relative amounts of the two ions. If a given amount of a replacing electrolyte is added to such an exchanger, Na will be replaced to a higher percentage, the lower the degree of saturation with Na. In case the ion exchanger is saturated with Na only, a minimum percentage of Na will be released, but when the degree of saturation falls, the replacement increases. As to K, on the other hand, the percentage release decreases with falling degree of saturation. Thus the replacement is maximal at saturation with K only.

Knowing the relative f-values of the ions it is possible to arrange the change in percentage replacement in falling direction at varying mutual saturation degrees of the following ion pairs:

$$\mathrm{Li} - \mathrm{K} > \mathrm{Na} - \mathrm{K};\ \mathrm{Mg} - \mathrm{Ba} > \mathrm{Ca} - \mathrm{Ba} > \mathrm{Sr} - \mathrm{Ba}.$$

Only in case all the adsorbed ions are homovalent and have equally great activity coefficients, the exchangeability will remain uninfluenced by the saturation degree. It appears from this that it is impossible to conclude from the nature of an ion whether its exchangeability decreases or increases with the degree of saturation, owing to the fact that this is determined not only by the ion in question but also by the nature and the relative amounts of the complementary ions.

7. With the support of point 5 and with the knowledge of the relative magnitude of the activity coefficients of the alkali and alkaline-earth ions one may assert that the exchangeability of an arbitrary ion grows in the order:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{La},$$

when these ions separately function as a complementary ion.

It may be pointed out here that the conclusions drawn from the formulas are valid even if the exchangeable ions are associated. In this case, however, the activity coefficient has to be calculated with regard to the degree of association in the way proposed by BJERRUM.

8. On account of the fact that in the formulas the volume of the micellar solution (v) is connected with the bivalent ions, the replacement of simultaneously appearing mono- and bivalent ions will be influenced by the concentration of the micellar solution. A low v-value, indicating a concentrated micellar solution, causes monovalent ions to be replaced to a relatively greater extent and bivalent ones to a relatively less extent than does a high v-value. Thus the phenomenon corresponds to the valence effect on dilution and to the effect exerted by the base exchange capacity upon the relative adsorption of Ca and NH_4 by soil minerals demonstrated by Mattson and Larsson (1946).

9. If an ion exchanger is saturated with mono- and bivalent ions, the replacement of the two ions will be very much dependent on the degree of saturation. Owing to the fact that the bivalent ions in formulas (19) and (21) enter with a square root expression, the percentage release of a monovalent ion will rapidly grow with falling saturation degree of this ion. If the calculation is made with Na and Ca, it will be seen from formula (21) that the percentage release of Na approaches its minimum when the saturation degree as to Na goes towards 100 ($D_{Na} \to 100$), but approaches its maximum when $D_{Na} \to 0$. $M_{Na} + M_{Ca}$ and R_T are supposed to be constant. On the other hand, it appears from formula (24) that owing to the fact that the monovalent ions enter with their squares, the release of a bivalent ion will decrease rapidly with falling degree of saturation. Contrary to what is the case with Na the percentage release of Ca approaches its maximum when $D_{Ca} \to 100$, but goes towards zero when $D_{Ca} \to 0$. The factor $\frac{k}{R_T \cdot v}$ may be considered to vary but little with the degree of saturation.

Some of the conclusions drawn above will be elucidated in the following by calculations according to the formulas presented. The computations are carried out for an exchanger saturated with two kinds of ions only at a degree of saturation varying for the two ions between 1 and 100 %. The replacing electrolyte is added in such a quantity that in one case 10 % and in the other case 50 % of the exchangeable ions are replaced. To make a calculation for such a high total replacement as 50 % is, theoretically, scarcely justified. In spite of this the computation shall be made, since it is of interest to get a comparison with the following experiments in which about 50 % were replaced. The kind of ions is varied by inserting different values for the activity coefficients of the ions

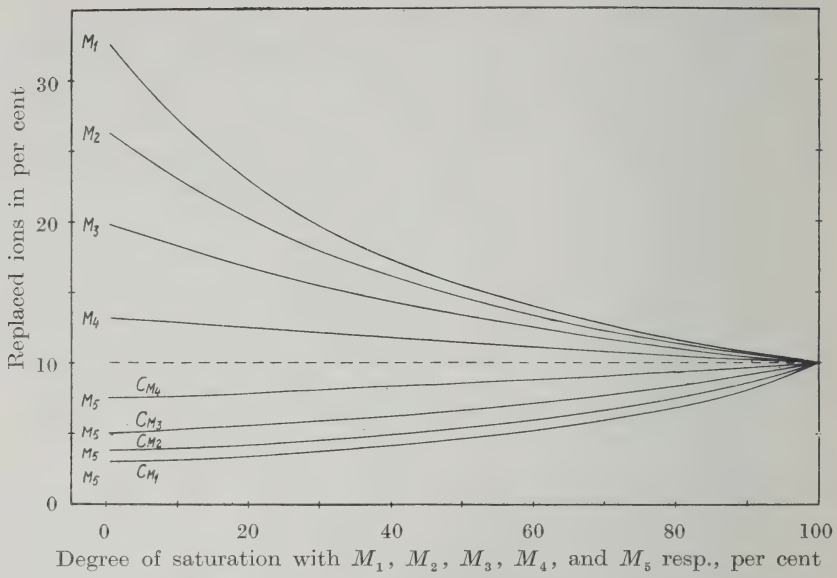


Fig. 32. Computed replacement of homovalent ions from an exchanger saturated with two ions: M_1-M_5, M_2-M_5, M_3-M_5, and M_4-M_5 resp. at mutually varying degrees. The f-values are supposed to be: $f_{M_1} = 1$, $f_{M_2} = 0.8$, $f_{M_3} = 0.6$, $f_{M_4} = 0.4$ and $f_{M_5} = 0.3$. Total replacement is constant and equal to 10 % of exchangeable ions. C_{M_1}, C_{M_2}, C_{M_3} and C_{M_4} denote that the complementary ions consist of M_1, M_2, M_3 and M_4 resp.

in the micellar solution (cf. fig. 32). The replacement of the homovalent ions is computed according to formula (20). The results are graphically presented in figures 32 and 33. It is to be noted that the total replacement of the two ions, calculated in per cent of the exchangeable ions or in m.e., is everywhere constant and not dependent on the varying proportions of the two ions. Further, it should be observed that the total exchangeable amount of the ions $M_1 + M_5$, $M_2 + M_5$, $M_3 + M_5$ etc. is constant. When the saturation with M_1, M_2, M_3 and M_4 resp. falls, the saturation of M_5 increases, so that:

$$D_{M_1} + D_{M_5} = D_{M_2} + D_{M_5} = D_{M_3} + D_{M_5} = D_{M_4} + D_{M_5} = 100\ \%.$$

From the curves in figure 32 it is evident that besides the nature of the ion studied the nature of the complementary ions and the degree of saturation exert a powerful influence upon the exchangeability of the ion. If the activity coefficients of the two ions are different, that is to say the replacing power of the ions are of different magnitude, the release of the ion with the higher f-value will

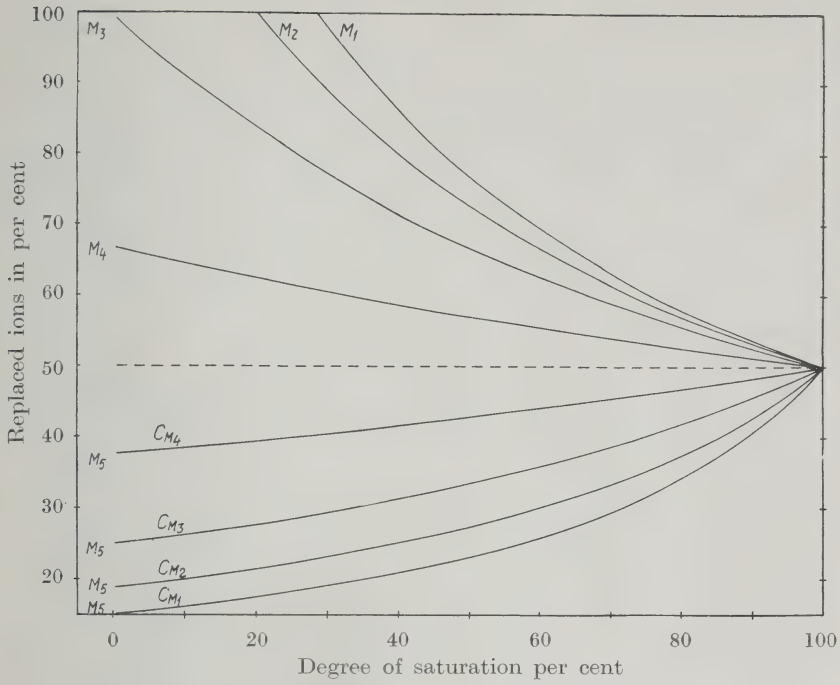


Fig. 33. The same as in fig. 32 but for the degree of replacement, which here amounts to 50 %.

increase but the release of the ion with the lower *f*-value will decrease with falling degree of saturation of the respective ion. This relation becomes the more marked the greater the difference between the *f*-values of the two ions. Thus it appears from the figure that the difference between the percentage replacement of the two ions grows in the order:

$$M_4 - M_5 < M_3 - M_5 < M_2 - M_5 < M_1 - M_5.$$

Only in that case when the *f-values* of the two ions *are equal* the percentage replacement will be *independent* of the degree of saturation. This case is represented in the figure by the dotted curve. It is to be seen that the slope of the M_5-curves is not as steep as the rise of the corresponding curves, which is explained by the fact that the total replacement is only 10 per cent.

When comparing figures 32 and 33 it appears that the relative increase and decrease of the replacement are considerably greater in case 50 % of the exchangeable ions are replaced than when only 10 % are replaced. Thus in the former case M_1 is completely replaced at $D_{M_1} = 24\,\%$, while in the latter case the replacement is

only 32.5 % at $D_{M_1} = 1\,\%$. Consequently, the change in the percentage replacement of an ion on variation of the degree of saturation becomes greater at high than at low replacement. Here it should be pointed out that, according to the Donnan equilibrium, a complete replacement of any ion is not possible with the experimental method applied here. As far as the concentration of an ion in the outside solution has not decreased to zero, this ion must also be found in the micellar solution though perhaps in a minute concentration (in the Donnan formula $z + y$ is always greater than x). The computed release of M_1 and M_2 in fig. 33 amounted to 100 % due to the fact that the formulas are not valid for computing percentage replacement approaching 100 per cent.

Calculations shall also be made with regard to the case that a monovalent ion is combined with a bivalent one. The total replacement is assumed to be 10 % and only two kinds of ions are included. In order to study the effect of varying concentration of the micellar solution on the replacement, four different v-values are considered. The replacement of the monovalent ion is computed from formula (21), the constant k being appropriately put to 0.47, and that of the bivalent by subtracting the former value from the total release. The results appear in figure 34.

It is evident from figure 34 that, under otherwise equal conditions, the replacement of a monovalent ion grows but that of a bivalent ion decreases with increasing concentration of the micellar solution or with increasing exchange capacity of the colloids. When the micellar solution successively grows more dilute, the replacement curves approach each other, which means that the valence effect tends to disappear. The effect exerted by the variation of the micellar concentration becomes most evident from the curves for the monovalent ions at the lower degrees of saturation. Naturally, the computed curves are of interest only from a qualitative point of view, since their shape changes with the k-value used.

Regarding the possibility to use the proposed formulas for quantitative calculations in real ion exchangers it must be stated that, unfortunately, this is impossible as long as the activity coefficients of the exchangeable ions are unknown. Still, the formulas are quite suitable for a qualitative analysis of the problems in question. In so far as it is possible either to determine experimentally or to calculate the activity coefficients in the micellar solution, the formulas can also be used for quantitative calculations. As to clay colloids also other factors than those mentioned here, e.g. fixation of added ions in nonexchangeable form, blockade effect, etc., can be supposed to influence the release of the adsorbed ions and, therefore, cause greater or smaller deviations from the formulas presented.

It is also interesting to examine somewhat more closely the variations which the activity coefficients of the exchangeable ions

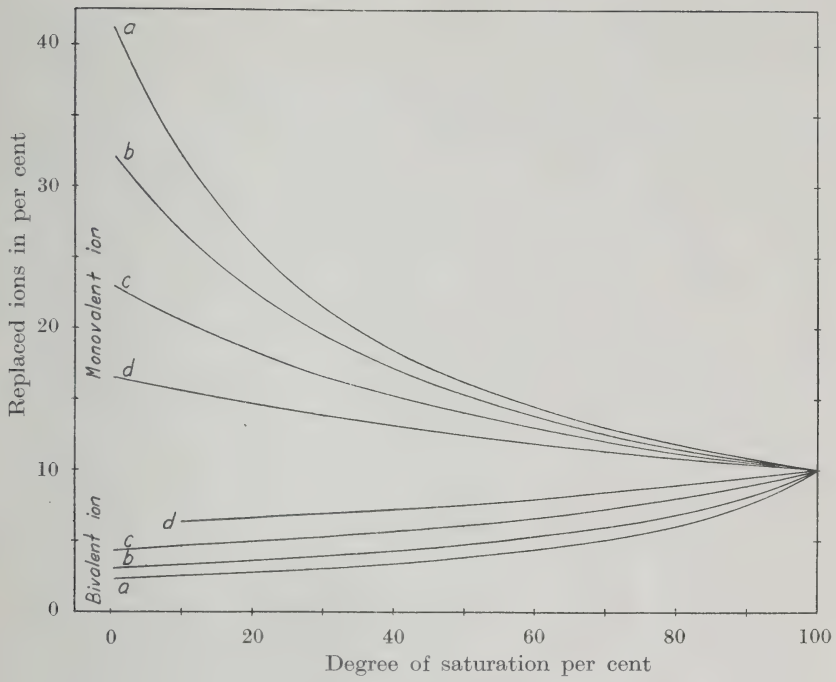


Fig. 34. Computed release of a monovalent ion ($f = 0.6$) and a bivalent ion ($f = 0.3$) at varying concentration of the micellar solution, the normality of which is in: $a = 3.3$, $b = 2$, $c = 1$ and $d = 0.5$. Total replacement equal to 10 % of exchangeable ions.

may undergo as a result of ion exchange and a change in the degree of saturation with the separate ions, since these conditions influence the mutual exchangeability of the ions and the validity range of the proposed formulas.

If a change in the composition of the ion swarm is accompanied by a change of the ionic strength in the micellar solution — in a certain degree, this is the case if the ions are heterovalent — the activity coefficients of the adsorbed ions may vary to some extent with the degree of saturation for the exchangeable ions. However, this variation can only be of a limited magnitude, because it is the charge of the ion exchanger itself that is the dominating factor for the f-values of the exchangeable ions. If, on the other hand, the charge of the ion exchanger is changed, the f-values, too, must vary. Such is the case if the adsorbed ions in a saloid from a weak acidoid are replaced by H-ions. By this, the charge of the ion exchanger decreases and, theoretically, at the same time, the activity coefficients of the adsorbed ions increase, giving rise to a valence

effect if the ions have dissimilar valence. If, on the other hand, the replacement is effected with the aid of a neutral salt, such a decrease of charge does not take place. If the ion exchanger is a strong acidoid, however, no decrease of charge occurs irrespective of the kind of the replacing ion. The formulas given above have been derived under the presupposition that the per cent release is small allowing the activity coefficients in the micellar solution and those of the replacing ions in the outside solution to be regarded as uninfluenced by the ion exchange. But the formulas are approximately valid even at greater replacement if only these latter conditions hold. It appears from what is said before that this should be the case for strong acidoids (e.g. the resin Wofatit K), the degree of protolysation of which is not changed when replacement takes place. Also saloids of weak acidoids approximately comply with the condition mentioned provided that the replacement is carried out with a neutral salt.

In the formulas no consideration is taken of the concentration of the replaced ions in the outside solution and the tendency of these ions to be re-adsorbed. This fact has little significance at low percentage replacement but, at high release, a greater or lesser error may appear. The error is due to the different increase of the activity coefficients of the ions when these are passing from the micellar solution to the outside solution, thus causing the re-adsorbing tendency of the ions to become unequal. The more different this increase of the f-values, the greater becomes the error; for heterovalent ions it will be more marked than for homovalent ions. On the other hand, the error becomes the smaller, the more dilute the outside solution, that is to say the lower the activity of the replaced ions in relation to that of the adsorbed ions.

3. Experimental Methods.

In order to verify the theories, experiments were made with exchangers saturated with two kinds of ions at mutually different degrees of saturation. However, the influence of a varying concentration of the micellar solution on the relative release of heterovalent ions could not be demonstrated since it was not possible to procure suitable ion exchangers of the same kind but with different exchange capacity. If for this purpose colloids are used which besides exchange capacity show dissimilarities also in other properties influencing the ion exchange, it may lead to the consequence that the effect of the different micellar concentrations becomes overshadowed by other possible factors.

In the experiments the following ion exchangers were used: the resins Wofatit K and Wofatit M, Vårdsberg clay, and the permutite described before. Because of the fact that the Wofatit K

mainly behaves as an »ideal» ion exchanger and because of its strong acidoid properties, by which its degree of protolysis did not vary during the experiments, it was particularly fit for the study of the problems in question. Therefore, most of the experiments were made with this material. The rest of the exchangers are but slightly protolysed in water.

For Wofatit K the following ion systems were applied: $Li—NH_4$, $Na—NH_4$, $K—NH_4$, $Mg—NH_4$, $Ca—NH_4$, $Ba—NH_4$, $La—NH_4$, $Ca—K$ and $Ca—Mg$,
for Wofatit M: $SO_4—Cl$,
for permutite: $Na—NH_4$ and $Na—K$,
for Vårdsberg clay: $Ca—NH_4$, $Ca—K$, and $Ba—Mg$.

Mg-, Ca-, and Ba-resins were prepared from the H-resin, to which a small volume of distilled water was added, by neutralization with a calculated amount of MgO, CaO and $Ba(OH)_2 + 8H_2O$ p. a. The flasks containing 250 g resin were shaken now and then for one month. Since Wofatit K is a strong acidoid, also MgO and CaO are dissolved in a comparatively short time. The equilibrium solution was found to be acid on addition of MR. After decanting, the resin was dried at 35—40° C. The contents of exchangeable ions were controlled by replacement with HCl.

La-resin was prepared by adding $LaCl_3$ in surplus to the H-resin. One day later the resin was transferred into a glass filter funnel and leached with additional $LaCl_3$ solution. After washing with CO_2-free distilled water until there was no reaction for chlorides, the resin was dried at 35—40° C. The contents of exchangeable La in the resin were determined by replacement with HCl.

The resins saturated with the other ions were not prepared in the ways mentioned; the ions were entered into the systems by neutralization of the H-resin and the OH-resin with hydroxide and acid respectively in the reaction flasks.

The experiments with Wofatit K were arranged in the following way. The H-resin and the resins saturated with metal cations were weighed into flasks and then the calculated volume of distilled water and hydroxide solutions were added. The amounts of adsorbed bases were calculated to equal 199.7 m.e./100 g dry H-resin. After 24 hours with repeated shaking, HCl equal to 400 % of the m.e. exchangeable bases was added. The total solution volume was everywhere 100 ml/6 m.e. added bases. By such an experimental method it was possible to keep constant the concentration of the exchanger in all the series as well as the total concentration of exchangeable ions and that of the replacing electrolyte. The only variable was the mutual degree of saturation, which varied for both of the ions in general between 10 and 100 %. The concentration of HCl was calculated to keep the total replacement somewhat above 50 %, which made the analytic results more reliable than in case

of a lower percentage replacement. After seven days with shaking for some hours every day, filtration took place, at which the first portion was discarded. In the filtrate the pH was determined by the glass electrode and analysis was carried out as to the contents of the two ions replaced.

In a few series some changes were made in the neutralization degree of the resin, but this will be treated in connection with the account of the experimental results.

The experiments with Wofatit M were carried out in a similar way. The Cl- and SO_4-ions were entered by neutralization of OH-resin with HCl and H_2SO_4 in the reaction flasks in an amount of the two ions equal to 167.6 m.e./100 g dry OH-resin. The total solution volume was 25 ml/m.e. acid added. After 24 hours with repeated shaking, NaOH equal to 60 % of the m.e. Cl- and SO_4-ions was added and then the procedure was the same as that mentioned above.

The permutite was electrodialysed for two months. Fractions between 0.2 and 0.6 mm were selected by sifting and used in the experiments. The H-permutite was saturated with Na, K and NH_4 by direct addition of the corresponding hydroxides into the reaction flasks. The contents of bases everywhere amounted to 60.0 m.e./100 g H-permutite and the solution volume to 30.0 ml/m.e. metal cations. After a shaking-time of four days an amount of HCl equal to 60 or 65 per cent of the cations entered was added. After another eleven days' shaking it was filtered through membrane filters (fine); the filtrate was analysed and pH determined.

The series with Vårdsberg clay was mainly carried out in the way described for the Wofatit K. The electrodialysed soil was neutralized in the reaction flasks with the calculated amounts of hydroxide. The appropriate degrees of saturation of the soil were obtained from the neutralization curves (fig. 25). The soil was saturated with 20.0 m.e. K and NH_4 resp., 23.0 m.e. Ca, and 24.0 m.e. Ba / 100 g H-soil. The Mg-soil was prepared in the same way as the La-resin. The contents of Mg were somewhat low and amounted only to 12.82 m.e./100 g H-soil. After 24 hours' shaking HCl equal to 60 % of the quantity of exchangeable cations was added. The total solution volume amounted to 50 ml/m.e. metal cations. After another seven days' shaking, it was filtered through membrane filters (fine); the further procedure was identical with that mentioned before.

Duplicates were often made with the different exchangers.

4. Analytical Methods.

A short description will here be given of the analytical methods which were applied for the determination of the different ions in

as much as they are not mentioned before. In case of great dilution of some filtrates as to a certain ion in a series, evaporation took place, so that all analyses in a series were made in equally large volumes. When the concentration of NH_4Cl, on account of the evaporation, grew very high, this salt was destroyed by fuming or by oxidation with aqua regia according to HILLEBRAND and LUNDELL (1929). In the filtrates from the series with soil and permutite, the SiO_2 was, when present, fumed away by means of hydrofluoric acid. The small amounts of the sesquioxides were then precipitated with NH_3 at pH 6, before the ensuing analyses.

In the filtrates from the Li-series, containing only NH_4Cl and HCl besides LiCl, Li was determined by addition of H_2SO_4 to the filtrate and evaporation to dryness; the ammonium salts were then fumed away. After cautious ignition, addition of H_2SO_4, and repeated ignition, the salt, Li_2SO_4, was weighed.

In the K-Ca-series reprecipitation of $KClO_4$ took place in case of high Ca-concentration and low K-concentration.

Before the determination of Mg in the Ca-Mg series, Ca was removed by precipitation as oxalate and then reprecipitation according to KOLTHOFF and SANDELL (1943), whose method aims to avoid co-precipitation of Mg. Mg was then analysed as mentioned before. In determining Ca reprecipitation was carried out in the systems containing small amounts of Mg, and two reprecipitations when the concentration of Mg was greater.

Before the analysis of Mg in the Ba-Mg series, Ba was removed by precipitation with H_2SO_4. Ba was estimated as $BaSO_4$ according to HILLEBRAND and LUNDELL (1929).

La was determined as $La_2(SO_4)_3$ by the addition of H_2SO_4 in surplus to the filtrate; evaporation followed and the ammonium salts were then fumed away. After that ignition up to 700° C ensued.

Sulphate was precipitated as $BaSO_4$. The solutions containing Na-ions in addition to SO_4- and Cl-ions were filtered through a column of H-saturated resin; at this all the Na-ions replaced H-ions, and the filtrates consequently came to contain only H_2SO_4 and HCl. H_2SO_4 was then determined by precipitation with $BaCl_2$. The contents of Cl were determined by precipitation with $AgNO_3$, followed by drying and weighing as AgCl according to HILLEBRAND and LUNDELL (1929).

5. Experimental Results.

In order not to burden the context with too many tables the results of the different ion exchange series have been summarized in a few tables, in which only the quantity of cations added and the percentage of ions replaced at the corresponding degrees of saturation have been recorded. The details given in Experimental

Methods enable, however, the reader to collect an exact information about the arrangement of the different series. When the results are presented graphically, the numbers of the figures are given in the tables. The degrees of saturation with the ions in question were generally made 100, 90, 70, 50, 30, and 10 % of the metal cations added. In every series the variation of the pH in the equilibrium solution was but inconsiderable and the pH-values are therefore not tabled.

A. *Replacement of cations from acidoid resin.*

The results from the different series are to be found in table 21.

a) *Series* $Li—NH_4$. As appears from table 21 and fig. 35 the release of NH_4 decreased but that of Li increased with falling degree of saturation. Below $D_{Li} = 30\,\%$ the replacement of Li grew rapidly. The fact that the release at $D_{Li} = 10$ became complete, may be due to the fact that Li was determined in a large volume of the filtrate and that the weighed Li_2SO_4 therefore contained small amounts of impurities emanating from the resin. The entire Li-curve would certainly have been steeper, if the release of Li at $D = 100$ had not amounted to 83 %. Considering that f_{Li} is appreciably greater than f_{NH_4} in not too dilute solutions, the result is in full agreement with the theory presented above.

b) *Series* $Na—NH_4$. The relation between replacement and degree of saturation for Na and NH_4 is similar to that for Li and NH_4 save for the fact that the slope of the curves is smaller. These conditions conform very well with the theory, since $f_{Na} : f_{NH_4} \simeq 1.51$ (calculated from f_{Na}, f_{NH_4} and f_K in part VII) and $f_{Li} : f_{NH_4} > f_{Na} : f_{NH_4}$.

c) *Series* $K—NH_4$. The release of NH_4 differs from that in the previous series by an increasing replacement with falling degree of saturation. On the other hand, the K-curve decreases somewhat when D_K diminishes. These conditions are in good agreement with the conception that the activity coefficient is in a high degree the determining factor for the relative exchangeability of an ion. In not dilute solutions $f_{NH_4} : f_K > 1$. As found in part VII this ratio in resin was 1.30.

d) *Series* $Mg—NH_4$

e) *Series* $Ca—NH_4$

f) *Series* $Ba—NH_4$

g) *Series* $La—NH_4$

It appears from table 21 and figure 36 that the replacement of NH_4 grows with falling degree of saturation. This relative increase of the replacement grows with the complementary ion in the order: $Mg < Ca < Ba < La$. As a matter of fact the activity coefficient of the complementary ions decreases in the same order. As may be expected, the release of Mg, Ca, Ba, and La at $D = 100$ lies in

Table 21. *The replacement of adsorbed ions on addition of HCl at varying degrees of saturation. Replaced ions in per cent of total amount of the ion in question. The resin saturated with 199.7 m.e./100 g dry H-resin.*

Series	Saturating ions	Degree of saturation in % of total added cations							Figures
		100 0	90 10	70 30	50 50	30 70	10 90	0 100	
a	Added Li m.e.	6	40.5	15.75	9	6.75	4.5	—	
Li–NH_4	» NH_4 m.e.	—	4.5	6.75	9	15.75	40.5	6	
	Replaced Li	83.4	84.4	85.5	87.2	89.7	100.7	—	35
	» NH_4	—	57.6	58.9	60.6	62.2	64.4	65.3	35,37
	$k_{Li:NH_4}$	—	0.25	0.24	0.23	0.19	—	—	
b	Added Na m.e.	3	40.5	12.6	6	2.25	1.5	—	
Na–NH_4	» NH_4 m.e.	—	4.5	5.4	6	5.25	13.5	—	
	Replaced Na	73.9	74.4	75.3	76.3	78.8	81.1	—	35
	» NH_4	—	60.0	61.7	63.0	64.3	64.7	65.0	35,37
	$k_{Na:NH_4}$	—	0.51	0.53	0.52	0.48	0.43	—	
c	Added K m.e.	6	0.5	15.75	9	6.75	4.5	—	
K–NH_4	» NH_4 m.e.	—	44.5	6.75	9	15.75	40.5	6	
	Replaced K	61.0	60.9	60.1	59.4	59.3	59.3	—	35
	» NH_4	—	68.1	67.3	66.9	66.2	65.3	65.0	35,37
	$k_{K:NH_4}$	—	1.37	1.36	1.38	1.35	1.29	—	
d	Added Mg m.e.	4.5	40.5	15.75	7.5	4.5	3	—	
Mg–NH_4	» NH_4 m.e.	—	4.5	6.75	7.5	10.5	27	—	
	Replaced Mg	49.3	47.9	44.5	40.5	36.0	32.2	—	36
	» NH_4	—	68.7	67.8	67.3	66.4	65.2	65.0	36,37
	$k_{Mg:NH_4}$	—	2.29	2.36	2.49	2.63	2.72	—	
e	Added Ca m.e.	6	40.5	15.75	10.5	9	6	—	
Ca–NH_4	» NH_4 m.e.	—	4.5	6.75	10.5	21	54	—	
	Replaced Ca	40.4	38.2	33.5	28.3	23.0	18.3	—	36
	» NH_4	—	71.7	70.8	69.5	67.4	65.6	65.0	36,37
	$k_{Ca:NH_4}$	—	3.22	3.42	3.63	3.78	4.02	—	
f	Added Ba m.e.	6	40.5	15.75	10.5	9	6	—	
Ba–NH_4	» NH_4 m.e.	—	4.5	6.75	10.5	21	54	6	
	Replaced Ba	31.1	27.3	20.7	15.2	10.9	6.7	—	36
	» NH_4	—	77.7	75.3	72.7	68.5	65.7	65.0	36,37
	$k_{Ba:NH_4}$	—	5.68	5.96	6.28	6.21	7.12	—	
g	Added La m.e.	7.5	40.5	21	15	11.25	7.5	—	
La–NH_4	» NH_4 m.e.	—	4.5	9	15	26.25	67.5	—	
	Replaced La	26.3	21.1	10.9	5.1	4.0	—	—	36
	» NH_4	—	84.1	81.9	77.2	69.9	65.5	65.0	36,37
h	Added Ca m.e.	6	40.5	15.75	12	9	6	—	
Ca–K	» K m.e.	—	4.5	6.75	12	21	54	—	
	Replaced Ca	40.4	38.9	34.1	30.4	25.4	20.6	—	
	» K	—	67.3	65.9	64.6	63.1	62.4	61.0	

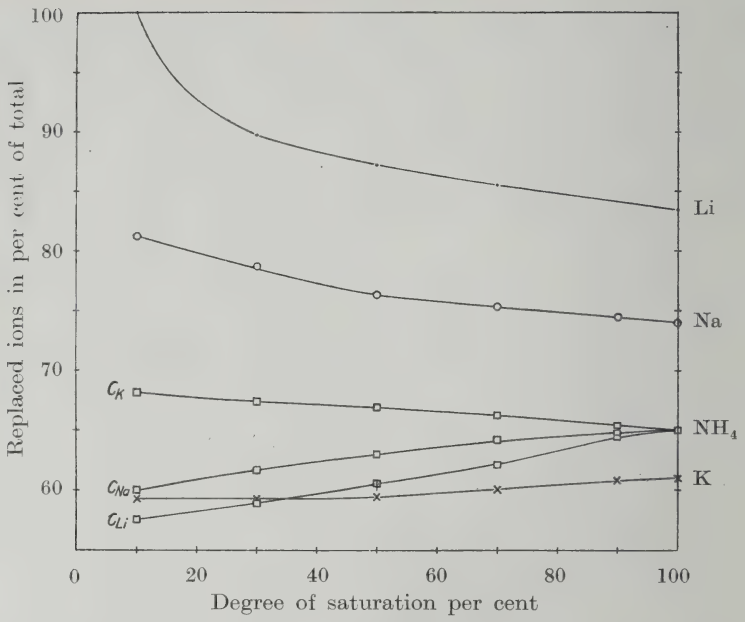


Fig. 35. The influence of the complementary ion and the degree of saturation on the release of Li, Na, K and NH_4 from resin, series a, b, and c, table 21, on addition of HCl. C_{Li}, C_{Na} and C_K denote the complementary ion of NH_4.

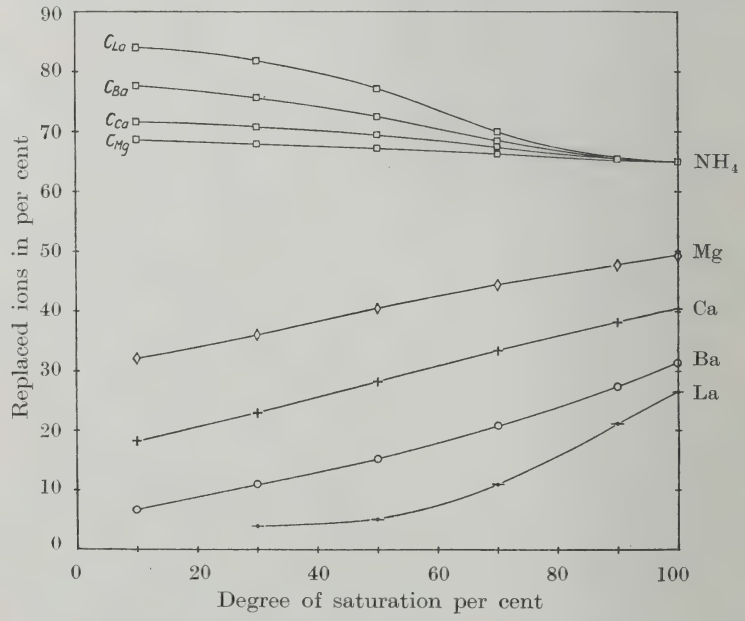


Fig. 36. Replacement of NH_4, Mg, Ca, Ba, and La from resin, series d, e, f, and g, table 21.

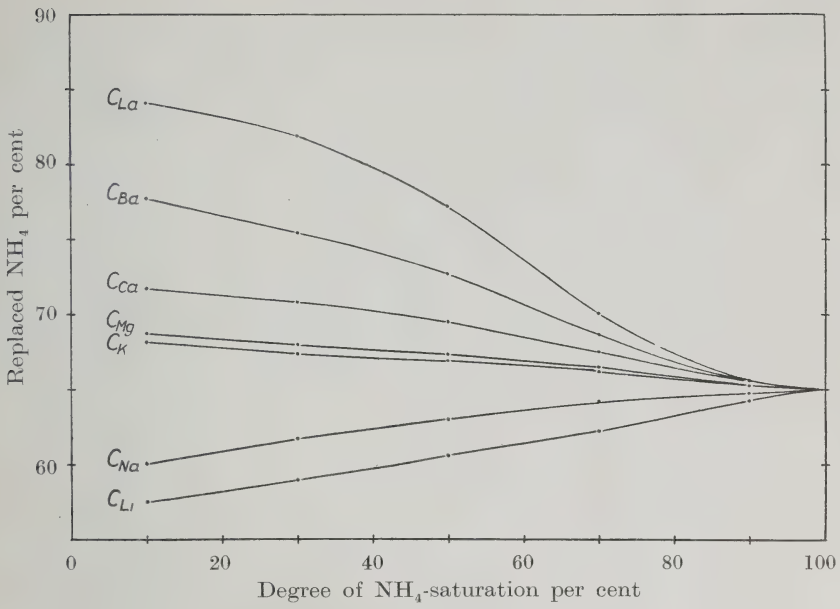


Fig. 37. The influence of the complementary ion and the degree of saturation on the release of NH_4 plotted from table 21. C_{Li}, C_{Na}, C_K etc. mean the complementary ions.

the reversed order and the percentage release diminishes with falling D in the sequence: Mg < Ca < Ba < La, which is in complete accordance with the theory.

h) *Series Ca—K.* In order to study if Ca—K would behave as Ca—NH_4, the former ion combination was also included. By comparing the series e) and h) in table 21 it appears that they gave similar results as was also to be expected. In agreement with the fact that K has a greater adsorption power than NH_4, the replaced amounts of K were smaller than those of NH_4 and the increase of the values was somewhat less for K than for NH_4. As a consequence of this the replacement curve of Ca was somewhat steeper in the Ca—NH_4 series than in the Ca—K series.

In fig. 37 the NH_4 released in the series $a—g$ is presented. In the figure it is very clearly shown that the nature of the complementary ion and the degree of saturation exercise a very great influence on the percentage release of an ion. When the f-value of the complementary ion, f_C, is less than the f-value of the ion studied ($f_{La}, f_{Ba}, f_{Ca}, f_{Mg}, f_K < f_{NH_4}$), the replacement curve of the latter rises, but when f_C is greater ($f_{Na}, f_{Li} > f_{NH_4}$) the curve descends with decreasing saturation. The relative effect of the ions included here

Table 22. *Replacement of K, NH_4, Mg, and Ca from resin saturated with K-NH_4, Ca-Mg and Ca-NH_4 resp. on addition of HCl.*

Series									
	Added K m.e.	9.695	69.80	27.15	15.51	11.63	5.817	—	Figu-
	» NH_4 »	—	5.476	8.214	13.69	26.01	49.28	6.845	res
i	Degr. of sat. K	100	92.7	76.8	53.1	30.9	10.6	0	
	» » » NH_4	0	7.3	23.2	46.9	69.1	89.4	100	
	Replaced K . . .	66.8	65.2	63.3	60.3	57.8	—	—	38
	» NH_4	—	—	69.8	67.4	64.8	61.9	60.9	38
j	Added Ca m.e.	7.935	57.13	22.22	11.11	9.522	6.348	—	
	» Mg »	—	5.444	8.166	9.527	19.05	49.00	6.805	
	Degr. of sat. Ca	100	91.3	73.1	53.8	33.3	11.5	0	
	» » » Mg	0	8.7	26.9	46.2	66.7	88.5	100	
	Replaced Ca . . .	50.9	50.1	46.9	42.1	40.4	37.6	—	39
	» Mg . .	—	68.2	63.7	61.0	—	53.8	51.8	39
k	Added Ca m.e.	7.2	48.6	18.92	14.4	10.8	7.2	—	
	» NH_4 »	—	4.0	5.50	10.0	17.0	42.3	5	
	Degr. of sat. Ca	100	92.4	77.5	59.0	38.8	14.5	0	
	» » » NH_4	0	7.6	22.5	41.0	61.2	85.5	100	
	Replaced Ca . . .	47.9	43.9	36.0	27.1	19.1	12.6	—	40
	» NH_4 .	—	75.9	72.6	68.5	62.9	58.7	55.1	40

on the exchangeability of the NH_4-ion has the following order: K<Na<Li; Mg<Ca<Ba<La. The effect of K is least and that of La greatest since $f_{NH_4} : f_K$ is nearest 1 but $f_{NH_4} : f_{La}$ widest from 1.

Besides the series given in table 21 three series were made, where the neutralization degree of the H-resin was varied with regard to the two ions. The total amount of the two exchangeable metal cations decreased successively from one end of the series to the other. The arrangement of the experiments as well as the results are shown in table 22 and figures 38, 39 and 40.

i) *Series K—NH_4.* The H-resin was saturated at $D_K = 100$ with 268.4 m.e. K and at $D_{NH_4} = 100$ with 179.6 m.e. NH_4 per 100 g dry matter. As is evident from table 22 and figure 38 the replacement of K at $D = 100$ became greater than that of NH_4. This is, however, explained by the fact that the neutralization degree as to K is much higher than with regard to NH_4. As was the case in series *c*, where the amount of K + NH_4 was constant, the replacement of K decreased but that of NH_4 increased with falling D; however, it is to be noticed that the decline of the K-curve as well as the rise of the NH_4-curve became considerably greater in series *i* than in *c*.

j) *Series Ca—Mg.* The H-resin was saturated at $D_{Ca} = 100$ with 209.7 m.e. Ca and at $D_{Mg} = 100$ with 180.3 m.e. Mg. Table 22, figure 39. In this series the degree of saturation influenced the replacement to a great extent. When $D = 100$ the difference be-

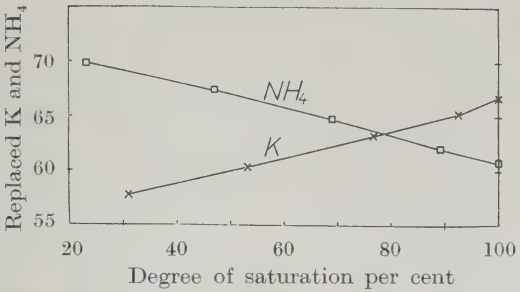


Fig. 38. The influence of the degree of saturation on the replacement of K and NH_4 from resin, series i, table 22.

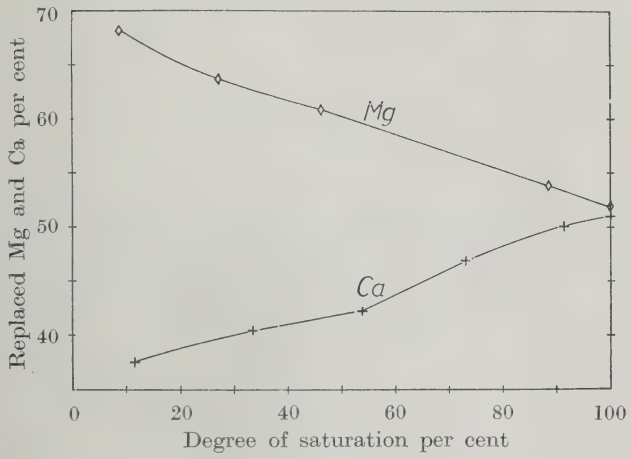


Fig. 39. Replacement of Ca and Mg from resin, series j, table 22.

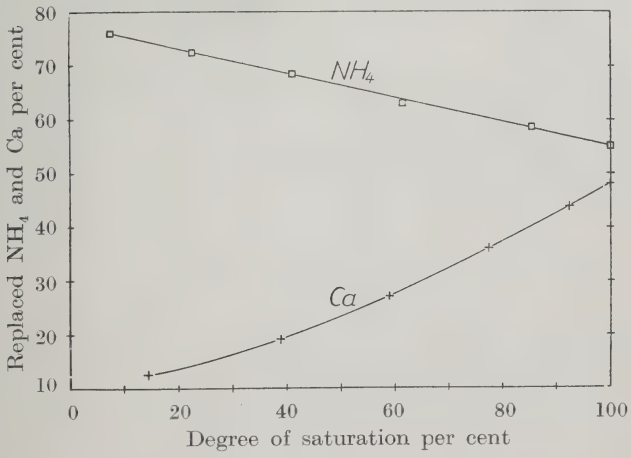


Fig. 40. Replacement of Ca and NH_4 from resin, series k, table 22.

tween replaced Mg and Ca was only 0.9 %, but when $D = 10$ the difference was about 30.6 %.

k) *Series Ca—NH_4.* The H-resin was saturated at $D_{Ca} = 100$ with 239.6 m.e. Ca and at $D_{NH_4} = 100$ with 133.1 m.e. NH_4. Table 22, figure 40. From the results in this series it appears that the replacement of NH_4 grew and the replacement of Ca decreased considerably more than in series *e*. Thus the NH_4-release was 20.8 % greater at $D = 7.6$ than at $D = 100$. The corresponding increase in series *e* was about 7 %. Consequently, the varying neutralization degree of the resin strongly influenced the release of NH_4 and Ca.

The following general conclusions concerning the release of adsorbed ions in the resin can be drawn from the results of the several ion combinations. The relative exchangeability of an ion, M_1, is dependent:

1. on its own nature,
2. on the degree of saturation with this ion,
3. on the nature of the complementary ion (M_2) and
4. on the degree of neutralization of the resin.

When the degree of M_1 saturation *decreases*, the exchangeability of this ion may increase, be unchanged, or decrease. What will happen is determined by the relative magnitude of the activity coefficients of the two ions. *The relative exchangeability will grow if $f_{M_1} > f_{M_2}$, it will be unchanged if $f_{M_1} = f_{M_2}$, and it will decrease if $f_{M_1} < f_{M_2}$.*

When $f_{M_1} > f_{M_2}$ and when the saturation degree of the resin with regard to M_1 (at $D_{M_1} = 100$ %) is less than with regard to M_2(at $D_{M_2} = 100$ %), the exchangeability grows more rapidly with falling D_{M_1} than when the saturation degree is equal. In the case of dissimilar valence of the ions, the increase or decrease of the exchangeability becomes greater than when the ions are homovalent.

Since it is possible to apply the law of mass action to the resulting distribution of cations between solution and exchanger in the experiments above, this will be done here for some of the series. The mass law, as it has generally been used, may be expressed for homovalent ions by the formula

$$\frac{M_{Na}}{M_K} = k_{Na:K} \cdot \frac{[Na]}{[K]} \text{ or } = k_{Na:K} \cdot \frac{M_{Na_o}}{M_{K_o}} \tag{25}$$

and for monovalent and bivalent ions by

$$\frac{\sqrt{M_{Ca}}}{M_K} = k'_{Ca:K} \cdot \frac{\sqrt{[Ca]}}{[K]}, \tag{26}$$

where bracket denotes concentration in the solution, M adsorbed amounts of the ions in m.e. respectively, k the exchange constant and o outside solution.

By comparing these formulas with the corresponding Donnan formulas in part VII, it appears that

$$k_{\mathrm{Na:K}} = \frac{f_{\mathrm{Na}_o} \cdot f_{\mathrm{K}_i}}{f_{\mathrm{K}_o} \cdot f_{\mathrm{Na}_i}} \text{ and } k'_{\mathrm{Ca:K}} = \frac{f_{\mathrm{Ca}_o}^{\frac{1}{2}} \cdot f_{\mathrm{K}_i}}{f_{\mathrm{Ca}_i}^{\frac{1}{2}} \cdot f_{\mathrm{K}_o} \cdot v^{\frac{1}{2}}},$$

where o and i signify the outside and the micellar solution respectively and v the volume of the micellar solution. If in formula (26) the concentration is substituted by the amount of cations in solution and the expression for k is inserted, the following general formula is obtained:

$$\frac{\sqrt{M_{\mathrm{Ca}}}}{M_{\mathrm{K}}} = \frac{f_{\mathrm{Ca}_o}^{\frac{1}{2}} \cdot f_{\mathrm{K}_i} \cdot V^{\frac{1}{2}}}{f_{\mathrm{Ca}_i}^{\frac{1}{2}} \cdot f_{\mathrm{K}_o} \cdot v^{\frac{1}{2}}} \cdot \frac{\sqrt{M_{\mathrm{Ca}_o}}}{M_{\mathrm{K}_o}} = k_{\mathrm{Ca:K}} \cdot \frac{\sqrt{M_{\mathrm{Ca}_o}}}{M_{\mathrm{K}_o}}, \qquad (27)$$

where V denotes the volume of the outside solution. It is to be noted that M and v refer to the same amount of the exchanger.

From the expressions above it appears that for monovalent ions k is not dependent on the volume of the micellar and outside solutions and that it is a real constant only if the activity coefficients do not change when the concentration is varied. Considering monovalent and bivalent ions, it is evident from formula (27) that the magnitude of k is determined in addition to the f-values by v and V. Still, V may be kept practically constant. As mentioned before, v changes with the character of the exchanger and even somewhat with the kind and concentration of the ions. Therefore, it is rarely possible to attain constants that are valid for different exchangers even if these have a homogeneous micellar solution and do not show any peculiarities in their exchange reactions. The variation of the activity coefficients allow the same conclusions. The k-value of a certain exchanger, in which all exchanging groups are accessible to the ions and which shows no specific reactions, can vary only to the extent that f, v and V change with a variation of the ion concentration. From what has been said, it is apparent that k must vary the less, the more similar the activity coefficients and the hydration of the ions.

The exchange constants have been computed for the ion combinations in series a—f in table 21 according to formulas (25) and (27). From the table the following appears:

1. The k-values for the monovalent ions change but slightly, despite the fact that the concentration ratios vary between 9:1 and 1:9. The change in k increase in the order: K-NH_4 < Na-NH_4 < Li-NH_4. As was to be expected $k_{\mathrm{K:NH_4}}$ is practically constant.

2. The change in k for monovalent and bivalent ions is greater, and increases in the order: $Mg\text{-}NH_4 < Ca\text{-}NH_4 < Ba\text{-}NH_4$.
3. k increases in the sequence: $Li < Na < K < Mg < Ca < Ba$, thus indicating a growing replacing power in the same order.

B. *Replacement of SO_4- and Cl-ions from basoid resin.*

The results from the exchange in the SO_4- and Cl-saturated resin are to be found in table 23.

Table 23. *Replacement of SO_4 and Cl in % of total from resin saturated with SO_4 and Cl in varying degrees. Replacing electrolyte was NaOH. Adsorbed SO_4 + Cl = 167.6 m.e./100 g dry OH-resin.*

Added SO_4 m.e.	5	27	14	8	6	4	—
» Cl »	—	3	6	8	14	36	4
Degr. of sat. SO_4	100	90	70	50	30	10	0
» » » Cl	0	10	30	50	70	90	100
Replaced SO_4	60.5	58.1	53.9	47.5	39.5	29.3	—
» Cl	—	75.1	74.9	73.4	71.3	66.1	62.9

From table 23 it is evident that the Cl-ions were replaced the stronger but the SO_4-ions the weaker, the lower the degree of saturation. It appears that even the exchange of anions from basoid resin follows the principles established for the cations in the acidoid resin.

C. *Replacement of cations from permutite.*

With this material two series were made, the ion combinations of which were: NH_4—Na and K—Na. The results are presented in table 24 and figures 41 and 42.

Table 24. *Replacement of NH_4, K and Na in % of total from permutite on addition of HCl. Adsorbed NH_4 + Na and K + Na resp. = 60.0 m.e./100 g H-permutite.*

Series									Figures
	Added NH_4 m.e.	4.8	10.8	6.3	4.8	2.7	2.4	—	
	» Na »	—	1.2	2.7	4.8	6.3	21.6	1.8	
a	Degr. of sat. NH_4	100	90	70	50	30	10	0	
	» » » Na	0	10	30	50	70	90	100	41
	Replaced NH_4	58.4	55.7	49.8	42.0	32.4	20.8	—	41
	» Na	—	89.6	85.3	81.8	76.7	69.3	64.5	
b	Added K m.e.	4.8	10.8	6.0	3.0	—			
	» Na »	—	1.2	4.2	15.6	1.8			
	Degr. of sat. K	100	90	58.8	16.1	0			
	» » » Na	0	10	41.2	83.9	100			
	Replaced K	53.7	51.5	38.7	18.4	—			42
	» Na	—	98.4	84.7	68.1	58.7			42

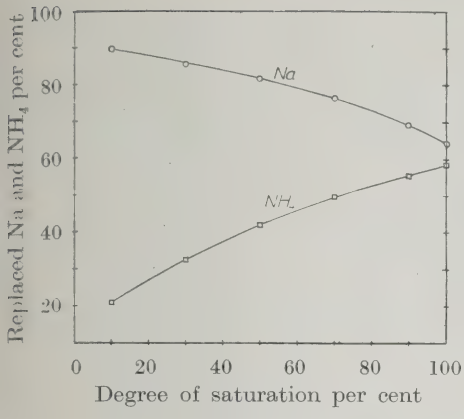


Fig. 41. The influence of the degree of saturation on the replacement of NH_4 and Na from permutite, series a, table 24.

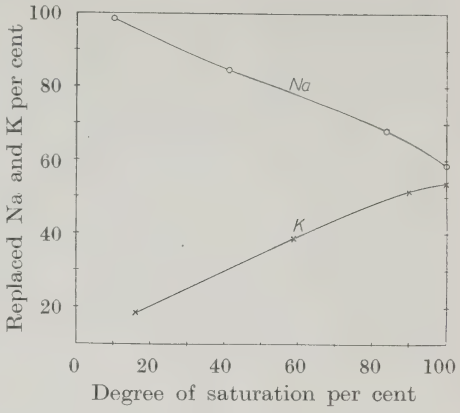


Fig. 42. Replacement of K and Na from permutite, series b, table 24.

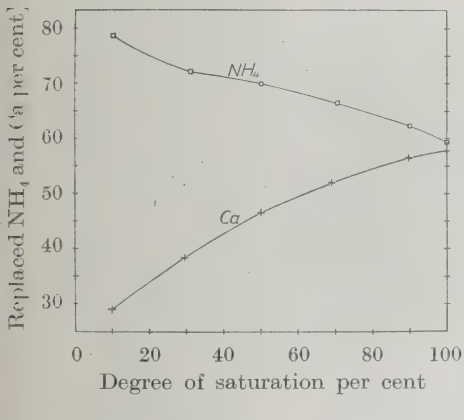


Fig. 43. The influence of the degree of saturation on the replacement of Ca and NH_4 from soil, series b, table 25.

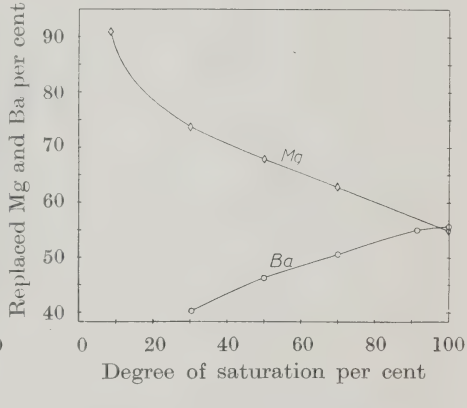


Fig. 44. Replacement of Ba and Mg from soil, series d, table 25.

a) *Series NH_4—Na.* HCl added in amounts of 65 % of adsorbed NH_4 + Na. As appears from table 24 and figure 41 the replacement of Na and NH_4 was greatly influenced by the degree of saturation.

b) *Series K—Na.* HCl added in amounts of 60 % of adsorbed K + Na. As shown from table 24 and figure 42 the Na-replacement increased by not less than 40 % when the degree of saturation was reduced from 100 to 10 %. On the contrary the release of K di-

minished by 35%, when D fell from 100 to 16%. It is of interest to compare the results from the two series. As may be expected, the Na-curve is steeper, when Na is combined with K than when combined with NH_4. In agreement with this the curve of K descended more rapidly than that of NH_4. These results are in harmony with the fact that $f_{Na} : f_K > f_{Na} : f_{NH_4}$.

D. *Replacement of cations from Vårdsberg clay.*

The results from the series the ion combinations of which were Ca—NH_4, Ca—K, and Ba—Mg, are presented in table 25 and figures 43 and 44.

Table 25. *Release of NH_4, K, Mg, Ca, and Ba on addition of HCl from Vårdsberg clay saturated with Ca—NH_4, Ca—K, and Ba—Mg respectively.*

Series									Figures
	Added Ca m.e.	2.3	12.19	4.6	2.3	2.3	1.84	—	
	» NH_4 »	—	1.40	2.0	2.4	5.6	17.40	2.0	
a	Degr. of sat. Ca	100	89.7	69.7	48.9	29.1	9.6	0	
	» » » NH_4	0	10.3	30.3	51.1	70.9	90.4	100	
	Replaced Ca	57.4	56.4	52.2	46.3	38.4	—	—	
	» NH_4	—	67.1	68.4	67.2	65.5	59.7	58.3	
	» NH_4 corrected for fixation	—	79.0	72.2	69.4	67.1	60.8	59.3	
	Added Ca m.e.	2.5	13.25	5.00	3.75	2.5	2.0	—	
	» NH_4 »	—	1.50	2.25	3.75	6.0	18.3	3.0	
b	Degr. of sat. Ca	100	89.8	69.0	50.0	29.4	9.9	0	
	» » » NH_4	0	10.2	31.0	50.0	70.6	90.1	100	
	Replaced Ca	57.7	56.4	51.9	46.5	38.3	29.1	—	
	» NH_4	—	67.2	68.2	67.5	64.4	60.9	57.9	43
	» NH_4 corrected for fixation	—	78.8	72.1	70.1	66.4	62.4	59.3	43
	Added Ca m.e.	—	17.48	6.44	3.45	3.45	1.84	—	
	» K »	—	2.00	2.80	3.60	8.40	17.40	2.4	
c	Degr. of sat. Ca	100	89.7	69.7	48.9	29.11	9.6	0	
	» » » K	0	10.3	30.3	51.1	70.89	90.4	100	
	Replaced Ca	57.7	57.8	55.5	51.6	44.0	32.5	—	
	» K	—	59.4	66.3	67.2	67.2	63.3	58.7	
	» K corrected for fixation	—	77.1	72.1	70.6	69.7	65.2	60.0	
	Added Ba m.e.	2.4	13.920	8.40	3.60	3.600	—	—	
	» Mg »	—	1.282	3.59	3.59	8.333	—	1.923	
d	Degr. of sat. Ba	100	91.6	70.1	50.1	30.2	—	0	
	» » » Mg	0	8.4	29.9	49.9	69.8	—	100	
	Replaced Ba	55.6	55.1	50.5	46.3	40.2	—	—	44
	» Mg	—	90.9	73.8	67.9	63.0	—	54.8	44

a) *Series Ca—NH_4.* At $D_{Ca} = 100$ the clay was saturated with 23.0 m.e. Ca and at $D_{NH_4} = 100$ with 20.0 m.e. NH_4. As shown in table 25 a, the relationship between the degree of saturation and the replacement of Ca and NH_4 was mainly the same as in the resin. NH_4 was the only exception at the lower degrees of saturation. When D fell below 50 the replacement increased but slowly, reached its maximum at $D = 30$, and then decreased somewhat. The explanation of this is probably that part of the added NH_3 must be supposed to be so strongly fixed by the organic matter of the soil that it is not directly replaceable with HCl. Even though such a fixation may be small, it will, however, cause a very much greater percentage decrease of the replaceable NH_3 at low degrees of saturation than at high degrees. As proved by MATTSON and KOUTLER-ANDERSSON (1943) humus is, under soil conditions, able to fix exchangeable ammonium to a considerable extent.

In order to find out to what an extent NH_3 is fixed by the Vårdsberg clay, the following experiment was carried out under conditions which as nearly as possible corresponded to those of the experimental series. To 8 g of soil distilled water and NH_3 corresponding to 20.0 m.e./100 g soil were added. The volume of solution added was 80 ml. After shaking for 24 hours, the ammonia was distilled with MgO. The average of two determinations showed a fixation of 0.35 m.e. NH_3/100 g soil. It is very probable that this value is less than if the replacement had been made with HCl as was the case in the experiments. On the other hand, the low ammonia concentration in the systems with low NH_3-saturation degrees will certainly cause a diminishing fixation. A correction of the NH_4-replacement values given in table 25 with regard to fixed ammonia will therefore be somewhat unreliable; still it is of interest from a qualitative point of view. It appears from the corrected values in the same table that the release of NH_4 grew with falling D in agreement with the theory.

b) *Series Ca—NH_4.* The preceding series was repeated, but with the modification that the soil was saturated with 25.0 m.e. Ca at $D_{Ca} = 100$ and with 15.0 m.e. NH_4 at $D_{NH_4} = 100$. The results appear from table 25 b and figure 43. The values corrected for NH_3-fixation are also recorded. The results in this series are very similar to those in series a. The slightly marked maximum of the NH_4-curve disappears after the correction. The fact that the neutralization degree was changed in the two series did not result in any obvious differences in the replacement values as in the case of the resin. This may be explained by the fact that, the clay having weak acidic properties, all added HCl was consumed by the exchange reactions, which was not the case in the resin.

c) *Series Ca—K.* The soil at $D_{Ca} = 100$ was saturated with 23.0 m.e. Ca and at $D_K = 100$ with 20.0 m.e. K/100 g H-soil. As

shown in table 25 c the results from the replacement of Ca and K are similar to those in the series with Ca and NH_4. The K release approaches a maximum and then decreases considerably. In order to account for this the possible fixation of K was studied. That K is often fixed in a nonexchangeable form is a well-known fact. The K fixation was studied in the following way.

To 10 g H-soil distilled water and 2.000 m.e. KOH were added. The suspension was shaken for 24 hours, whereafter HCl equal to 60 % of the KOH was added. The total solution volume was 111.8 ml. After shaking for a week, the soil — up to this time treated as in the experiments — was leached on a filter with 300 ml 0.5 N. NH_4Cl in small portions. After fuming away dissolved SiO_2 with HF, the filtrate was analysed for K by precipitation with $HClO_4$. As an average of two determinations the value of fixed K amounted to 0.54 m.e./100 g soil.

From the table it is evident that the correction of the K-replacement values resulted in the disappearance of the maximum and a distinct increase of the values.

d) *Series Ba—Mg.* The H-soil was saturated with 24.0 m.e. Ba at $D_{Ba} = 100$ and with 12.82 m.e. Mg at $D_{Mg} = 100$. Table 25 d and figure 44. The falling degree of saturation led to a very marked increase (36 %) of the Mg-replacement and a corresponding decrease of the Ba-replacement. This is in good agreement with the theory and with the results from the resin.

6. Conclusions.

As it appeared from the experiments, the results from the many different ion exchange series showed a qualitatively good agreement with the theories presented in spite of the great difference in nature of the ion exchangers. The acidoid and basoid resins as well as the permutite and the mineral soil behaved in the same way: The percentage replacement of an ion is dependent partly on *its nature*, partly on *the nature of the complementary ions*, and partly on *the degree of saturation* with the ions in question. If the mutual replacing power of two ions is different, the exchangeability of the ions may decrease or increase with a change of the relative proportions of the ions. If the ions are heterovalent, an additional factor will be the valence effect as governed by the concentration of the micellar solution. The present study shows, both by theory and by experiments, that the widely accepted conclusion that the exchangeability of an ion is decreased by the presence of complementary ions is far from having general validity. While this conception applies to certain of the adsorbed ions, it does not apply to the others, the relationship being governed by the factors discussed above.

The results obtained are of interest from many points of view and this is especially true of the nutrients in the soil. When only very small fractions of the exchangeable ions are removed from the soil particles, as is usually the case in the soil, the theory should apply well.

In many soils the nutrients are leached out more or less. In view of the fact that the exchangeability of an ion is determined by the above-mentioned factors, it is evident that the ions should be leached out to a varying extent under different conditions. In normal soils the complex is principally saturated with Ca which has a great replacing power as compared to that of some of the other exchangeable ions. As a consequence of the complementary ion principle and the effect exerted by the degree of saturation, Ca should become the more difficult to displace, the lower the Ca-saturation. On the other hand, the ability of Na to be leached out is greater at a low degree of saturation than at a high one, which probably explains the generally low Na contents in soils. Mg and K will take an intermediate position.

Such factors as the relative contents of exchangeable ions, the degree of saturation, and the concentration of the micellar solution which have proved to be of importance on the replacement of adsorbed ions, naturally enough, will also influence the adsorption of ions on addition of electrolytes. On irrigation with saline water these factors must consequently be of importance for judging the ensuing adsorption and replacement processes. The importance of the degree of base saturation in this connection is to be seen in an experiment by AYRES (1941). On percolating two Hawaiian soils of various Ca—H-saturation degrees with 0.001, 0.01 and 0.1 N. KCl, the K-adsorption from the 0.1 N. solution increased strongly with growing Ca-saturation. This is probably due to a greater replacing power of H than of Ca in the two soils. However, in 0.01 N. solution the increase was less and in 0.001 N. only slight, which for the rest may be interpreted as a marked consequence of the valence effect on dilution.

Considering the great influence which in the present experiments appeared to be exerted by the kind of the complementary ion and the degree of saturation on the exchangeability of a certain ion, one might expect that the availability of nutrients to plants should also be affected by these factors. However, it will be difficult to decide exactly to what an extent a variation of the relative exchangeability of the adsorbed ions in the soil might be reflected in the contents of the plants of the nutrients in question. According to LUNDEGÅRDH (1942) plant roots possess such a strong absorption energy with regard to nutrients that the retarding power of soil colloids is of little or no importance.

Most probably the adsorption of ions by soil colloids is but one of the many factors which affect the uptake of nutrients and

determine the amounts of these contained in the plant. If the relative magnitude of the factors shows variations in different soils, the complementary ion effect may make itself felt in certain cases but not in others. On the other hand, a change of the degree of saturation may be expected to yield a more pronounced effect. In this connection the studies on uptake of nutrients and on growth as made by HORNER (1936), YARUSSOV (1938), and MARSHALL (1944 b) are of special interest. HORNER found that the Ca-absorption by soy-beans increased with a growing degree of Ca-saturation at a constant Ca-level. He was also able to establish that the ability of the plants to take up Ca is affected by the amount and the replacing power of the other adsorbed ions. Analogous results were obtained by YARUSSOV in experiments with beans. The results of both the authors are in good agreement with the conclusions, to be drawn from the experiments discussed above, concerning the influence of the complementary ions and the degree of saturation on the availability of an ion. However, the results obtained by MARSHALL indicate that the complementary ion principle does not always govern the uptake of nutrients; as pointed out above, this result is to be expected.

In a recent paper MEHLICH and COLWELL (1946) have demonstrated that peanuts absorb more Ca from kaolin-sand mixtures than from montmorillonite-sand mixtures at the same Ca-level and degree of saturation of the two minerals. Similar results have previously (1943) been found with cotton and soybeans. These results are interesting for the present investigation, because they support the theory that the concentration of the micellar solution affects the relative exchangeability of heterovalent ions, cf. fig. 34. According to this, Ca should be more easily replaced from kaolin than from montmorillonite, since the former mineral has a more dilute micellar solution than the latter. In consequence, the plants are able to take up more Ca from kaolin than from montmorillonite.

Certain investigators appear to have confused the conceptions: exchangeability of an ion, suitably expressed as percentage replacement, and the quantities of the ion in question available for the plants. Irrespective if the exchangeability of an ion decreases, remains unchanged, or grows with falling degree of saturation, the total exchangeable amount of the ion naturally decreases and, by this, the possibility for the plants to satisfy their needs, in case the degree of saturation diminishes. If for instance the contents of exchangeable K in the soil drop to a tenth of the original value, the exchangeability may remain unchanged or probably grow a little. For the plants, however, it will be much more difficult to take up a certain quantity of K since in the latter case the contents of the complementary ions in relation to K have become 10 times greater and, by this, their competitive power with regard to the

exchanging ions, which are active in the process of nutritive uptake, has increased by about 10 times. In order to absorb the same amount of K the plant must therefore produce much more carbon dioxide at the lower K-saturation degree than at the higher degree of saturation.

An interesting problem to be discussed in the light of the results found here is the effect which a neutralization of an acid soil by liming may exert upon the exchangeability of the nutrients. JENNY and AYERS (1939) assert that a substitution of Ca for H in the soil should render K more available. On the contrary BRAY (1942) vindicates that such a substitution must result in a decreasing relative release of the other ions.

Concerning this problem one can maintain that, paradoxically enough, either conceptions may be correct in certain cases but incorrect in other cases. No formula and no single experiment can give a definite answer to this question since the conditions may vary from soil to soil. This is explained by the fact that the replacing power of the H-ion in relation to that of the Ca-ion varies with the nature of the soil colloids. As proved by SCHACHTSCHABEL (1940) H has a less replacing power than Ca in montmorillonite. In many other materials the opposite conditions hold as demonstrated above. Consequently, in a montmorillonitic soil a replacement of H with Ca should, according to the theory presented, be followed by a greater exchangeability of the complementary ions. On the other hand, when the H-ion is more strongly adsorbed than Ca, an exchange of H for Ca should cause a decreasing exchangeability of the other ions and, theoretically, render them more unavailable to plants as far as this factor is concerned in the uptake of the nutrients.

On account of the complementary ion principle and the effect of the degree of saturation, the time necessary for complete replacement of an ion is dependent in a high degree on the kind of the active ion. Adsorbed ions, the adsorption intensity of which is lower than that of the replacing ion, are rapidly removed, while adsorbed ions with an adsorption intensity greater than that of the active ion are the more difficult to remove, the lower the degree of saturation. Being weakly adsorbed in strong acidoids (cf. part V) the H-ion is therefore no ideal replacing agent in such an exchanger. In weak acidoids, on the other hand, the H-ion is very effective in displacing adsorbed ions.

Continued investigations into the problems discussed here are planned, especially concerning the exchange conditions at very low degrees of saturation, the effect exerted by varying concentration of the micellar solution on the exchangeability of heterovalent ions, the replacement conditions when hydrogen is the complementary ion, and the exchange conditions on replacement with ions other than hydrogen.

X. Summary.

Part II.

A distinction has been drawn between the concept of the crystallographic ionic radius and that of the radius of the hydrated ion. The ion hydration theory of Fajans and Born is presented. The hydration increases with the charge of the ion and decreases with growing crystallographic radius. The most probable hydration numbers of several ions are tabled.

The activity concept for electrolytes has been discussed as far as it has a bearing on the problems dealt with in this paper. The relationship between activity coefficient (f) and ionic strength (μ) according to Debye and Hückel as well as the ion association theory of Bjerrum have been briefly treated.

At the discussion of the micellar structure the theories of Helmholtz, Gouy, and Stern have been touched. Besides, an account has been given of the highly varying structure of the ion exchangers and the importance of this fact to the exchange reactions. The concepts of »outer-surface» and »inner-surface» ion exchange as well as ion blockade have been dealt with.

The clay colloids principally consist of crystalline silicates belonging to the mineral groups of montmorillonite, kaolinite, and mica. A description has been given of the structure of these minerals and of some of their properties. The clay minerals are not statical but show transitions, which are due to their continuous subjection to disintergration and formation caused by the pedogenic factors, giving a dynamic character to the soil complex.

The base- and acid-binding power of the soil complex may be considered localised to acidic and basic groups respectively, which form the surface complex and impart amphoteric properties to soil colloids. The base-binding power may be attributed partly to the »broken bonds», which result from breaks in the crystal followed by an interaction with water molecules, partly from lattice ion substitution resulting in the formation of free negative charges, and partly from the acidic function of silicic acid, carboxyl and phenol groups. The acid-binding power, on the other hand, is confined partly to amphoterically functioning aluminium- and ferri-aquo-groups and partly to aminogroups. A picture of the surface complex is given.

The strength of acidoids and basoids as well as ampholytoids has been discussed. The protolysation of the acidic and basic groups may be assumed to be governed by the same laws which are valid for ordinary acids and bases. The course of the neutralization curve is determined partly by the pk-values of the acidic groups, the intensity-factor, partly by the actual amount of these groups, the capacity-factor.

In giving an account of the application of the activity concept to colloids the great importance of the ion activity in the study of ion exchange reactions has been specially emphasized, while on the other hand the activity of the electrolyte is a matter of secondary significance only.

A close study has been devoted to the qualitative application of the Donnan equilibrium to ion exchange. It has been emphasized that the replacing power and the resulting distribution of the ions are intimately dependent partly on the ionic valence, partly on the relative reduction of the activity coefficients of the ions, when these pass from the outside to the inside solution, and partly on the ratio of the activity of the micellar solution and that of the outside solution.

Part III.

In the introduction it has been pointed out that the relative H-ion replacing power of the cations can, under certain conditions, be studied by adding neutral salts with common anion to the H- and OH-saturated colloids.

Theoretical considerations on ionic exchange showed that, when neutral salts are added to an »ideal» acidoid, the exchange acidity for the following ions ought to have the order:

$$Li < Na < K < Mg < Ca < Sr < Ba < La.$$

Exceptions may occur in true acidoids and ampholytoids by

(a) the fact that the structural conditions of the exchanger cause ion blockade,
(b) specific reactions between the salts and the exchanger such as fixation of cations, lattice ion exchange, dissolution etc. and
(c) an »abnormal» variation of the activity coefficients of certain ions.

The materials investigated consisted of humus, synthetic silicates and phosphates, soil minerals, and soils in a H- and OH-saturated condition.

Solutions of the salts Li-, Na-, K-, Mg-, Ca-, Sr-, Ba-, and La-chloride in the concentrations 0.001, 0.01, 0.1 and 1 N. were added to the exchangers. After 24 hours the pH was electrometrically determined in the suspension or the centrifugate. On certain exchangers neutralization curves were made.

Studies of the velocity of the ion exchange between H-permutite and H-humus and KCl and $MgCl_2$ showed that pH remained practically unchanged either the determinations were made immediately or 24 hours after the addition of the salt.

The experiments showed that the *relative pH-reducing power* of the alkali and alkaline-earth ions varies considerably according to the *nature* of the ion exchanger, the *concentration* of the salt and the *degree of neutralization* of the acidoid. On the whole, humus behaves like an »ideal» acidoid, while some of the mineral colloids show particularly great deviations. At the lowest concentrations the bivalent ions, as a rule, decrease the pH more than the monovalent ones; on the other hand, inverse conditions often prevail at higher concentrations. Thus in the ferrisilicate in 1 N. solution the following order was obtained for the pH-reducing effect: Mg < Sr < La < Ca < Li < Ba < Na < K.

In the montmorillonitic soils KCl yielded very strange pH-curves which differed considerably from the curves of the other salts. It is not possible to advance a general order of the replacing power or the pH-reducing effect of cations, since these properties can vary strongly with the nature of the exchangers and the concentration of the salts.

Part IV.

Two ion exchange resins, a sulphonic cation exchanger, Wofatit K, and an anion exchanger, Wofatit M, were studied.

Wofatit K was examined as to:

1. its contents of the elements S, Fe, and N;
2. how quickly it gets completely soaked in water;
3. whether in H-saturated status it disengages acidic substances on percolation with water;
4. its mechanical stability when shaken in water;
5. the time required for reaching exchange equilibrium;
6. its capacity of binding bases at different pH.

The experiments showed, among other things, that the dissolution of acidic substances from the resin is very minute, that a small but noticeable quantity of acidic substances gets in solution on shaking, and that the exchange equilibrium is attained after 40—80 minutes.

Wofatit M was examined as to:

1. its contents of nitrogen;
2. the stability on leaching with distilled water;
3. the capacity to bind HCl and H_2SO_4 in water and in solutions of NaCl and Na_2SO_4;
4. the pH in KCl and K_2SO_4 solutions.

Wofatit M is not completely stable in distilled water but disengages minute amounts of NH_3. The capacity of binding H_2SO_4 in water is greater than that of binding HCl. On the other hand,

in 1 N. NaCl the resin binds more HCl than H_2SO_4 in 1 N. Na_2SO_4. These problems have been discussed in the light of the activity concepts.

Part V.

The study on the relative order of the replacing power of the more common cations has here been continued with studies on the position of the H-ion in relation to that of the other ions. On theoretical considerations it has been shown that the relative replacing power of the H-ion is in the first line a function of:

a) the ratio between f_H in the outside and inside solutions in relation to the same ratio of the other ions present.

b) the strength of the acidoid.

With the activity coefficient and the hydration number of the H-ion as a basis it was possible to determine its relative position in the lyotropic series. *In an acidoid completely protolysed in water the H-ion occupies no exceptional position having a replacing power determined by the same factors as for the other ions.* On the basis of the theoretical considerations in part II, for such an acidoid we arrived at the following series for the replacing power:

$$Li < H < Na < K < Mg < Ca < Sr < Ba < La.$$

For incompletely protolysed acidoids, the H-ion moves more to the right, the weaker the acidoid.

The problem has been experimentally elucidated by comparing the amounts of NH_4-ions replaced by different chlorides from the resin Wofatit K, a permutite, a clay, and an ordinary bath sponge, all in the NH_4-saturated conditions.

The experimental results were in full agreement with the theoretical conclusions drawn here. For the resin, which is a strong acidoid, the mutual replacing power of the ions coincided with the order mentioned above. For permutite, clay and sponge the relative replacing power of the H-ion increased in the order the materials are mentioned as a consequence of the decreasing acidoid strength.

Part VI.

The amphoteric reactions of a H- and OH-saturated ampholytoid on the addition of a series of salts of the type M_2A, in which the cations possess different replacing power, have been discussed. The inferrence was reached that the exchange alkalinity forms a maximum and that it should grow larger and the maximum point should be displaced towards a higher salt concentration when the replacing power of the cation decreases.

The conclusions drawn have been verified by experiments with aluminium phosphate and the salts Li_2SO_4, Na_2SO_4 and K_2SO_4.

Part VII.

The effect of dilution on the exchange equilibrium in the resins Wofatit K and Wofatit M has been studied.

Three essentially different methods have been applied. The results obtained showed:

a) that the exchange equilibrium between H—Li, H—Na and H—K is, at the concentration here used, not influenced by a 25-fold dilution and that the same applies to NH_4—K at 10000-fold dilution and that the adsorption of Li compared to the adsorption of Na and K is increased when the concentration grows from 0.1 N. to 1 and 4 N.

b) that the equilibrium between H—Mg, H—Ca, H—Ba and Cl—SO_4 at 25-fold dilution is displaced markedly, and between NH_4—Ca at 10000-fold dilution very strongly towards an increased adsorption of the bivalent ion.

Moreover, the experiments showed that in the acidic resin the H-ion replacing power of the following ions has the same order as for an »ideal» acidoid, viz.:

$$Li < Na < K < Mg < Ca < Ba.$$

Considering the results attained some practical problems were discussed.

Part VIII.

The effect of heating on the exchangeability of the adsorbed ions in permutite and in a clay has been studied. Na-, K-, Mg- as well as Ca-saturated permutite and K- and Ca-saturated Vårdsberg clay, all suspended in water, were heated on a steam bath for 48 hours, whereafter the exchangeability of the ions with HCl was studied and compared with the exchangeability in unheated samples. The time of reaction was 0.5, 5, 50, and 86 hours.

From these experiments it appeared that the exchangeability in the heated permutite decreased in the order: $Na < Ca < K < Mg$.

The difference between K and Mg was small, but between these ions and Ca considerable. Na was replaced much more easily than the rest of the ions. In the clay, too, heating caused a marked reduction of the exchangeability of the adsorbed ions, and this was the case to a higher extent with K than with Ca.

The velocity of the ion exchange in permutite varied according to the kind of the saturating ion in the order: $Mg < Ca < K < Na$.

The direct effect of the heating on the ion exchanger was discussed briefly and the fact was pointed out that high temperatures may lead to the consequence that calculations of the ion exchange equilibrium become unreliable or faulty.

Part IX.

In this part there is a brief discussion on the general conception of decreasing exchangeability of any ion with a decrease in the degree of saturation of the colloids with the ion in question, irrespective of the nature of the other adsorbed ions, i.e. the complementary ions. On the basis of the law of mass action and of the activity concept some formulas for computing the release of adsorbed ions have been deduced.

From the formulas it was possible to conclude that the replacement of an ion by any other ion is dependent partly on the activity coefficients (f) in the micellar solution of all the exchangeable ions, partly on the relative amounts (degree of saturation, D), and partly on the total amount replaced. If the adsorbed ions are heterovalent, the release is to some extent dependent also on the concentration of the micellar solution.

The formulas and the curves computed from these show that the percentage replacement of an arbitrary ion (M_1) may *increase*, be *unchanged* or *decrease* when the degree of M_1 saturation falls. The percentage replacement of M_1 increases if $f_{M1} > f_C$ (f_C = activity coefficient of the complementary ion of the same valence), it is unchanged if $f_{M1} = f_C$ and it decreases if $f_{M1} < f_C$. If the adsorbed ions are heterovalent, the percentage release of the ion of lower valence will increase but that of the ion of higher valence will decrease with a decrease in the degrees of saturation. The per cent release of a monovalent ion decreases but that of a bivalent ion increases if the concentration of the micellar solution diminishes, other conditions being equal.

At any degree of saturation the percentage replacement of an arbitrary cation grows in the order:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{La},$$

when these ions separately act as a complementary ion.

The theory was studied by experiments with four different ion exchangers: acidoid resin, basoid resin, permutite, and mineral soil. The exchangers were saturated with two kinds of ions — in all twelve different ion combinations — the mutual amounts of which varied in general from 100 to 10 %.

In spite of the very different nature of the ion exchangers, the many ion combinations gave results in good agreement with the theory. The influence of the complementary ions and of the degree of saturation on the exchangeability of the ions was very markedly demonstrated.

The use of the law of mass action for exchange reactions was discussed and the exchange constants for some ion combinations were computed.

In connection with the results obtained certain points of view on the behaviour of the ions towards leaching have been discussed as well as the availability of nutrients to plants and the effect of liming on the exchangeability of ions.

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